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IMPROVED MOLECULAR COLLISION MODELS FOR
NONEQUILIBRIUM RAREFIED GASES

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Abstract

The Direct Simulation Monte Carlo (DSMC) method typically used to model thermochemical nonequilibrium rarefied gases requires accurate total collision cross sections, reaction probabilities, and molecular internal energy exchange models. However, the baseline total cross sections are often determined from extrapolations of relatively low-temperature viscosity data, reaction probabilities are defined such that experimentally determined equilibrium reaction rates are replicated, and internal energy relaxation models are phenomenological in nature. Therefore, these models have questionable validity in modeling strongly nonequilibrium gases with temperatures greater than those possible in experimental test facilities. To rectify this deficiency, the Molecular Dynamics/Quasi-Classical Trajectories (MD/QCT) method can be used to accurately compute total collision cross sections, reaction probabilities, and internal energy exchange models based on first principles for hypervelocity collision conditions. In this thesis, MD/QCT-based models were used to improve simulations of two unique nonequilibrium rarefied gas systems: the Ionian atmosphere and hypersonic shocks in Earth’s atmosphere.

The Jovian plasma torus flows over Io at ≈ 57 km/s, inducing high-speed collisions between atmospheric SO$_2$ and the hypervelocity plasma’s O atoms and ions. The DSMC method is well-suited to model the rarefied atmosphere, so MD/QCT studies are therefore conducted to improve DSMC collision models of the critical SO$_2$-O collision pair. The MD/QCT trajectory simulations employed a new potential energy surface that was developed using a ReaxFF fit to a set of \textit{ab initio} calculations. Compared
to the MD/QCT results, the baseline DSMC models are found to significantly under-predict total cross sections, use reaction probabilities that are unrealistically high, and give unphysical internal energies above the dissociation energy for non-reacting inelastic collisions and under-predicts post-dissociation SO internal energy. Implemented into DSMC, the MD/QCT-based models had a significant effect on simulations of simple, thermal nonequilibrium heat bath and 2D counterflow cases approximating the upper atmospheric conditions of Io. In high-fidelity 1D simulations of the atmosphere of Io, the MD/QCT models predicted approximately half the SO$_2$ atmospheric dissociation due to O and O$^+$ bombardment and a temperature rise due to plasma heating further from the Ionian surface than the existing baseline methodologies.

Hypersonic spacecraft re-entering Earth’s atmosphere experience significant heating from the post-shock gas. The DSMC method is used to model hypersonic shocks during the early stages of re-entry because of the rarefied nature of the atmosphere at high altitudes. Improved modeling of the N-N$_2$ and N$_2$-N$_2$ collision pairs are thus generated with MD/QCT. For the N-N$_2$ pair, a potential energy surface developed at NASA Ames is used and, for the N$_2$-N$_2$ pair, a new potential energy surface is developed using a ReaxFF fit to recent advanced *ab initio* computations. The MD/QCT-computed total cross sections agreed well with the baseline models, but the MD/QCT reaction probabilities exhibited better physical behavior, a stronger dependence on initial molecular internal energy, and were generally lower than the baseline DSMC chemistry models for strong nonequilibrium conditions, but higher for equilibrium conditions. Furthermore, the MD/QCT results predicted faster rotational-translational energy relaxation for the N-N$_2$ pair and faster vibrational-translational energy relaxation for the N$_2$-N$_2$ pair. The
MD/QCT models were tested in DSMC simulations of 2D axisymmetric hypersonic flow over a blunt body and thermal nonequilibrium heat bath cases. The MD/QCT models led to increased post-shock $\text{N}_2$ dissociation and faster rates of internal energy relaxation, each of which led to corresponding decreases in translational temperature.
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Nomenclature

Roman Symbols

$\bar{E}_b$  Average internal energy of bin $b$

$\bar{n}_b$  Thermal weight associated with bin $b$

$\bar{Q}$  Global bin model partition function

$\bar{Q}_b$  Internal energy partition function within bin $b$

$\bar{v}_b$  Average vibrational level of bin $b$

$b$  Internal energy bin index

$B_{max}$  Maximum impact parameter

$d$  Intermolecular distance

$D_e$  Molecular dissociation energy

$d_{ref}$  VHS total cross section reference diameter

$E_\Lambda$  Arrhenius activation energy

$E_c$  Total collision energy

$E_i$  Internal energy

$E_{rot}$  Rotational energy

$E_t$  Translational energy
$E_{vib}$ Vibrational energy

$f(c_r)$ Relative velocity distribution function

$f(E_i)$ Continuous internal energy distribution function

$g_b$ Degeneracy of bin $b$

$g_i$ Degeneracy of energy level $i$

$k_B$ Boltzmann constant, $1.38065 \times 10^{-23}$ J/K

$k_r$ Reaction rate

$k_{de}$ Bin de-excitation rate

$k_{ex}$ Bin excitation rate

$M_i$ Mass of atom $i$

$n$ Number density

$N_s$ Number of trajectories resulting in process $s$ in an MD/QCT case

$N_T$ Number of trajectories in an MD/QCT case

$N_{NR}$ Number of non-reacting trajectories in an MD/QCT case

$p_{i,j}$ Atomic momentum for atom $i$, direction $j$

$P_{inel}$ Inelastic collision probability

$Q_{rot}$ Rotational partition function

$Q_t$ Translational partition function
\( r_{i,j} \) Atomic position for atom \( i \), direction \( j \)

\( T_a \) Temperature controlling reaction in Park two-temperature model

\( T_{coll} \) Collision temperature

\( T_{int} \) Rovibrational, or internal, temperature

\( T_{ref} \) VHS total cross section reference temperature

\( V \) System potential energy

\( Z_R \) Rotational relaxation collision number

\( Z_V \) Vibrational relaxation collision number

\( Z_{R,eff} \) Effective rotational relaxation collision number

**Greek Symbols**

\( \chi_i \) Deflection angle in MD/QCT trajectory \( i \)

\( \eta \) Arrhenius exponent parameter

\( \Lambda \) Arrhenius pre-exponential factor

\( \mu \) Reduced mass

\( \nu \) Vibrational frequency

\( \omega \) VHS total cross section viscosity exponent

\( \sigma_{\nu,MD} \) Viscosity cross section

\( \sigma_{coll,MD} \) Non-reacting collision cross section
\( \sigma_{ref} \) VHS total cross section at \( T_{ref} \)

\( \sigma_{s,MD} \) Cross section for process \( s \)

\( \sigma_{tot,MD} \) Total cross section

\( \sigma_{VHS} \) VHS total cross section

\( \theta_v \) Characteristic temperature of vibration

\( \zeta_i \) Total internal degrees of freedom

\( \zeta_{rot} \) Rotational degrees of freedom

\( \zeta_{vib} \) Vibrational degrees of freedom

\( \epsilon_{int,i} \) Dimensionless change in target internal energy in MD/QCT trajectory \( i \)

**Subscripts**

\( A, B \) Bin indices for molecules A and B

**Other Symbols**

\( ' \) Post-collision value

\( * \) Intermediate value
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Chapter 1

Introduction

1.1 Modeling Nonequilibrium Rarefied Gases

The ability to accurately simulate rarefied gases has important and ranging implications, from improved predictions of heating on hypersonic spacecraft to greater understanding of outer planetary atmospheres. It is well known that numerical solutions of the Navier-Stokes equations give excellent predictions of continuum gas behavior. However, the Navier-Stokes equations are only accurate while the continuum assumption holds. The degree of gas rarefaction can be quantified by the Knudsen number, $Kn = \frac{\lambda}{L}$, where $\lambda$ is the mean free path and $L$ is a characteristic flow length scale. For finite and increasing $Kn$, the continuum assumption breaks down as the shear stress and heat flux terms fail to be expressed in terms of macroscopic transport parameters.

At sufficiently high velocities, the thermal and chemical time scales of a gas can become approximately on the same order of magnitude as the flow time scale. In such cases, finite rate chemistry contributes significantly to the thermal and chemical description of the gas. Additionally, the distributions of molecular rotational and vibrational energies deviate from a Boltzmann distribution corresponding to the bulk gas translational temperature. These gases are referred to as nonequilibrium gases.

Transitional and rarefied gas regimes can only be accurately modeled through particle-based simulations, which can be applicable for nonequilibrium flows. However,
full-scaled molecular dynamics is not feasible for spacecraft re-entry or planetary simulations due to the extreme computational cost associated with modeling all the system atoms and molecules. An alternative approach is the Direct Simulation Monte Carlo (DSMC) [4] method, which simulates the Boltzmann equation that governs gases ranging from continuum to free-molecular conditions. The DSMC method has been successfully employed in a wide range of applications, including flows through microstructures, granular gases, initial upper atmosphere re-entry flight, and rarefied planetary atmospheres. However, the underlying physical models in DSMC are often not reliable for strongly nonequilibrium gases. This is particularly true for the two systems that motivate the research in this thesis: flows around early-phase re-entry space vehicles and atmospheric simulations of Io, a moon of Jupiter.

1.1.1 The Atmosphere of Io

The atmosphere of the Jovian moon Io has been the source of significant scientific interest since its discovery by the Pioneer spacecraft in 1973 [16, 17]. The atmosphere is significantly altered by day/night and eclipse effects, and contributions to its composition include: sublimating $\text{SO}_2$ surface frosts, volcanism that expels a significant amount of $\text{SO}_2$, and interaction with Jupiter’s magnetosphere and plasma torus. The atmosphere primarily consists of $\text{SO}_2$ and daughter species components $\text{O}_2$, $\text{SO}$, $\text{S}$, and $\text{O}$. Initial simulations of Io by Wong and Johnson [18], Wong and Smyth [19], and Smyth and Wong [20] assumed a continuum atmosphere and solved the Navier-Stokes equations. However, Io’s atmosphere is rarefied and therefore its overall character can not be reliably predicted by traditional continuum computational fluid dynamics. As such,
Pospieszalska and Johnson [21] used 1D Monte Carlo simulations to model Io's atmosphere due to ion-induced sputtering. More recently, the computational approach of choice has been the Direct Simulation Monte Carlo (DSMC) [4] method. Comprehensive planetary physics modeling through the use of DSMC by Austin and Goldstein [22], Zhang et al. [23, 24, 25], Moore et al. [26, 27, 28, 29], Walker et al. [30, 31, 32], and Gratiy et al. [33, 34] has been ongoing at The University of Texas and Penn State University to study the complex phenomenology of Io's energetic, but rarefied, atmosphere.

Accurate SO$_2$ collision models are critically important in DSMC simulations of the Ionian atmosphere. This is particularly true for collisions between atmospheric SO$_2$ and O$^+$ and S$^+$ ions from the Jovian plasma torus that flows over Io at $\approx 57$ km/s [17]. Because the O and S neutral atoms have effectively the same mass as their ionized counterparts, it is assumed that they have similar collision dynamics with SO$_2$ molecules. The high-velocity ions contribute a significant amount of energy to Io's atmosphere via collisions with its neutral constituent gas particles, which may be ionized, dissociated, and heated. The energetic neutrals and ions created by plasma interaction above the exobase can escape Io and re-supply the torus [35, 36, 37]. Some energetic neutrals and ions may even reach the Ionian surface and induce sputtering of surface material [38, 21].

1.1.2 Hypersonic Earth Re-entries

Spacecraft entering planetary atmospheres experience significant heating as the high speed vehicle transfers kinetic energy to the surrounding gas. Accurate prediction of these thermochemical processes is critical to the understanding of these flows, which are important for spacecraft aerodynamics predictions and design of the heat
shield. Typically, for low speed flows, gas chemistry is in equilibrium and its composition can be determined by only the local temperature. However, at sufficiently high speeds, such as those observed in Lunar or Martian returning spacecraft, the gas thermal and chemical timescales are approximately on the same order of magnitude as the flow time scales, rendering the equilibrium assumption invalid. In these cases, chemical, vibrational, rotational, and electronic relaxation, ionization, and radiation effects are significant contributors to the description of the flowfield. Further, these thermochemical processes are strongly coupled to one another. For Earth re-entries, these phenomena particularly relate to molecular nitrogen N$_2$, a dominant component of the Earth’s atmosphere. The quality of numerical predictions of these flows is tied directly to the accuracy of the physical model for the nonequilibrium processes. Comparison of simulations with limited flight experiment data, such as the Stardust re-entry [39, 40, 41] or the FIRE II flight experiment [42, 43, 44, 45], or ground-based experimental shock-tube data [46, 9, 10, 11, 12] is possible. High-altitude, hypersonic reentry flight is characterized by high Knudsen numbers and is therefore often modeled using the direct simulation Monte Carlo (DSMC) [4] approach because of its ability to represent, with high-fidelity, thermochemical nonequilibrium flows. However, individual atomic/molecular collision models must be based on rigorous chemical physics methods, as comparison with experimental data is only for highly averaged quantities such as heat flux, pressure, and sometimes spectra.
1.2 The Direct Simulation Monte Carlo (DSMC) method

The Direct Simulation Monte Carlo (DSMC) [4] approach is a probabilistic particle simulation method used to solve the Boltzmann equation, typically for high Knudsen number flows. In DSMC, the computational domain is divided into cells and filled with simulation particles that represent molecules of different chemical species, and boundary conditions are imposed. Each simulated particle represents a large number of real atoms or molecules. DSMC is based on the dilute gas approximation that states that the continuous process of particle movement and interactions are uncoupled, and every particle is moved according to its velocity and acceleration at each time step. Therefore, the time step is chosen such that the mean time between particle collisions is well-resolved and the mean free path limits cell sizes such that particles generally move only a fraction of the cell during a timestep. At each time step, only collisions between particles belonging to a given cell are taken into account, which are considered as random events with some probability of occurring. Binary collision models determine the probability of a collision for a given particle pair, and also determine the appropriate particle internal energy exchange, chemical reaction, and post-collision particle velocities, while ensuring energy conservation. After steady flow is attained, the pertinent macroparameters (temperatures, pressure, etc.) are sampled within each computational cell and is usually conducted over many time steps in order to minimize statistical error. DSMC is unconditionally stable, but it is noted that computational expense increases with the number of simulated particles.
1.2.1 Total Cross Section Models

The probability of a collision between a particle pair in DSMC is related to the collision cross section. The variable hard sphere (VHS) [4] and variable soft sphere (VSS) [47, 48] models are most commonly used in DSMC and have the form,

\[
\sigma_{VHS} = \sigma_{\text{ref}} \left( \frac{2k_B T_{\text{ref}}}{\mu c_r^2} \right)^{\omega - 1/2} \frac{\Gamma \left( \frac{5}{2} - \omega \right)}{\Gamma \left( \frac{5}{2} - \omega \right)},
\]

where \( c_r \) is the relative velocity. The reference cross section, \( \sigma_{\text{ref}} \), reference temperature, \( T_{\text{ref}} \), viscosity exponent \( \omega \), and reduced mass \( \mu \) are specific to each species collision pair. The general hard sphere (GHS) [49] and general soft sphere (GSS) [50, 51] have also been developed to model the total cross section in DSMC. Each of these models each use parameters specific to a collision pair, which are determined such that experimentally developed macroscopic transport parameters are replicated, such as viscosity. However, for high temperatures such as those observed in hypersonic flight, reliable experimental transport data does not exist. Therefore, the validity of cross sections based on lower temperature viscosity data is unknown. Furthermore, each of these models depend only on the relative translational energy between colliding particles. It is generally assumed that the collision cross section is independent of collision pair internal energies, however, the validity of this assumption is not well understood. Thus, a collision model not based on low-temperature experimental data and with consideration towards molecular internal energies represents a significant improvement over the mentioned methods.
1.2.2 Chemistry Models

The well-known Arrhenius form of chemical reaction rates used in continuum gas dynamic simulations is not applicable to DSMC. Therefore, the commonly used total collision energy (TCE) [4] was developed to determine reaction probabilities in DSMC that, under equilibrium conditions, reproduce reaction rates in the Arrhenius form, which is given as,

$$k(T) = \Lambda \eta \exp \left( \frac{-E_{\Lambda}}{k_B T} \right),$$

(1.2)

where the $\Lambda$, $\eta$, and $E_{\Lambda}$ parameters are specific to a given reaction path. However, the problems with the TCE model are two-fold. First, while the TCE model may reliably reproduce Arrhenius rates under equilibrium conditions, they may not accurately describe reaction chemistry in nonequilibrium flows. It is well-known that many dissociation reactions are more likely for vibrationally excited molecules [3, 52, 53, 54]. Therefore, when a gas is in vibrational nonequilibrium, inherent uncertainty in the TCE model arises. Further, the Arrhenius rates are generally obtained as fits to experimental data. Again, experimental data have a limited temperature range. In re-entry, hypervelocity collisions corresponding to temperatures above those possible in a laboratory setting are expected. Therefore, Arrhenius rates are determined based on extrapolations of lower-temperature data. The validity of probabilities based on these extrapolated rates are unknown.

To address the vibrational favoring of dissociation reactions, Haas and Boyd [55] introduced the vibrational-favored dissociation (VFD) model, which placed an additional dependence of reaction probability on a favoring parameter $\Phi$. This parameter effectively gave molecules with higher vibrational levels a higher reaction probability. However,
there exists uncertainty in the selection of the empirical parameter $\Phi$ due to the limited information on the degree of vibrational favoring.

The recently developed simple, phenomenological Quantum-Kinetic (QK) approach of Bird [8, 56] gives DSMC diatomic dissociation probabilities dependent on quantum vibrational numbers and relies on the assumption that diatomic molecules can be modeled as simple harmonic oscillators. Consider a collision with total collision energy $E_c$, which is the sum of the relative translational energy and the combined pre-collision molecular internal energies. For a diatomic modeled as a harmonic oscillator with characteristic vibrational temperature $\theta_v$, the maximum vibrational level that can be selected is

$$v_{\text{max}} = \frac{E_c}{k_B \theta_v}.$$  

(1.3)

The potential post-collision vibrational levels, $v^*$, are selected from a uniform distribution of the set of states less than or equal to $v_{\text{max}}$ using the acceptance-rejection technique with probability

$$P = \left(1 - \frac{v^* k_B \theta_v}{E_c} \right)^{3/2} - \omega,$$

(1.4)

where $\omega$ is the VHS viscosity exponent from Eq. 1.1. Then, a dissociation reaction occurs if

$$v^* > \frac{k_B E_d}{\theta_v},$$

(1.5)

where $E_d$ is the dissociation energy. The QK reaction rates were found to agree well with reaction rates for various air species collision pairs. However, again, these rates are
determined under equilibrium conditions. Moreover, the validity of the harmonic oscillator assumption is diminished for the expected highly vibrationally excited molecules that may be expected in high-temperature gases, where anharmonicity effects become significant. As such, the QK model does not accurately predict high-lying vibrational populations, and because vibrationally excited molecules can contribute significantly to high-temperature dissociation, this leads to a loss in accuracy in predicting dissociation probabilities. Furthermore, Prof. Bird acknowledges that modern theories of gas-phase chemical reactions based on accurate potential energy surfaces may provide better physical representation of the dissociation processes [8].

1.2.3 Internal Energy Relaxation Models

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. The most commonly used internal energy exchange method is the Larsen-Borgnakke [57] (LB) model, which describes vibrational-translational (VT) and rotational-translational (RT) energy transfer and determines post-collision internal energy from a continuous equilibrium Maxwell-Boltzmann internal energy distribution. The equilibrium relative translational energy distribution function is [58]

$$ f_{E_t} \propto E_t^{3/2} -1 \exp \left( \frac{-E_t}{k_B T} \right) $$

(1.6)
where $\zeta_t$ is the relative translational degrees of freedom for the collision pair defined by [4]

$$\zeta_t = 5 - 2\omega,$$

(1.7)

where $\omega$ is the viscosity exponent from Eq. 1.1. Similarly, the continuous equilibrium distribution function for internal energy of a molecule $E_i$ with $\zeta_i$ internal degrees of freedom is [59]

$$f_{E_i} \propto E_i^{\zeta_i/2-1} \exp\left(-\frac{E_i}{k_B T}\right),$$

(1.8)

where $\zeta_i = \zeta_{rot} + \zeta_{vib}$. The rotational degrees of freedom, $\zeta_{rot}$, are defined as,

$$\zeta_{rot} = 0 \text{ for atoms},$$

$$\zeta_{rot} = 2 \text{ for diatomics and linear polyatomics},$$

(1.9)

$$\zeta_{rot} = 3 \text{ for non-linear polyatomics},$$

and the vibrational degrees of freedom for internal energy, $\zeta_{vib}$, assuming a simple harmonic oscillator approach, are given as,

$$\zeta_{vib} = \frac{n\theta_v / T}{e^{\theta_v / T} - 1}, \quad n = \text{number of atoms in molecule}.$$  

(1.10)

For a polyatomic molecule, the vibrational modes are usually lumped together, giving one effective vibrational energy mode and thus not partitioning the energy into each vibrational mode [57]. Boyd [60] and Bergemann and Boyd [61] extended the phenomenological LB approach to simulate RT and VT energy exchange for diatomics, respectively,
assuming discrete internal energy distributions for each. Gimelshein et al. [62] 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. 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 [63] for $Z_R$ and Millikan and White [64] 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 nonequilibrium conditions and, second, at sufficiently high temperatures, it predicts molecular internal energies much greater than their respective bond energies and are therefore unphysical.

The Schwartz, Slawsky, and Herzfeld (SSH) [65] model for determining vibrational-translation (VT) relaxation rates was derived for non-rotating harmonic oscillators with simple, repulsive potentials and parameters chosen to replicate experimental data. However, its validity is called into question due to the use of an *ad hoc* intermolecular potential. More recently, the analytic FHO-CR model [66] for simulating internal energy relaxation in diatomic molecules has been designed for applicability to hypersonic rarified flows. The model, which is based on extensions of earlier iterations referred to as
the FHO [15] and FHO-FR [67] models, is able to predict probabilities of single-quantum and multi-quantum vibrational and rotational transitions. However, it is based on a relatively simple Morse-based intermolecular potential and has weak coupling between the rotational and vibrational levels, which neglects the centrifugal force in rotationally excited molecules that affects the vibration potential [2] and, thus, the vibrational energy relaxation process.

1.3 The Molecular Dynamics/Quasi-Classical Trajectory (MD/QCT) Method

Various models have been presented for collision cross sections, chemical reactions, and molecular internal energy exchange in DSMC. The limitations on these models generally arise from derivation assumptions and extrapolating low-temperature parameters to strong thermal nonequilibrium conditions, such as those observed in hypersonic spaceflight or in some planetary atmospheres. The molecular dynamics/quasi-classical trajectory (MD/QCT) method can be used to generate collision cross sections, reaction probabilities, and internal energy exchange models. MD/QCT uses classical mechanics to deterministically simulate individual binary collisions between gas-phase molecules or atoms using Hamilton’s equations. It is applicable for adiabatic collisions in which the Born-Oppenheimer approximation may be invoked [68], which reduces the computation of a binary collision from solutions of the Schrödinger equation to those of nuclear motion on a potential energy surface. The accuracy of gas properties resulting from the MD/QCT method are therefore directly tied to the fidelity of the potential energy
surface (PES) used. PESs are generally an analytic representation of spectroscopic experimental data or quantum mechanical calculations. Quantum mechanical methods can approximate the solution of the Schrödinger equation and thus give accurate electronic structure and inter-atomic force representation of a given system. Batches of trajectories are run for initial $v, J$ quantum states and relative velocities, and results are partitioned for final $v', J'$ states, thus giving the quasi-classical trajectory name. Cross sections are then proportional to the fraction of trajectories that end up in a given state. Therefore, collision, reaction, relaxation, and state-to-state specific cross sections can be determined and provide the basis for collision, chemistry, and internal energy exchange models.

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

\[
\dot{p}_{i,j} = -\frac{\partial V}{\partial r_{i,j}} \tag{1.11}
\]

\[
\dot{r}_{i,j} = -\frac{p_{i,j}}{M_i} \tag{1.12}
\]

where $V$ is the system potential, $p$ is atomic momentum, $r$ is atomic position, $M$ is the atomic mass, $i$ is the atomic index, and $j$ is the direction index. In this work, Hamilton’s equations are solved using a fourth-order Runge-Kutta method that is described in detail in Appendix A.

Each case in an MD/QCT study consists of a large set of trajectories defined by common pre-determined relative collision velocity, $c_r$, and initial molecular internal energies. The individual trajectories within a case have unique impact parameters, target molecular orientations, and may also have unique partitions of internal energy, each of
which are determined using the efficient microcanonical sampling method detailed in Appendix B in order to obtain statistically significant resulting cross sections.

Upon completion of an MD/QCT trajectory simulation, the interatomic distances of the system particles determine which, if any, reaction has occurred. If a given system atom is more than 3.0 Å from the nearest atom, that atom is determined to be unbound with any other atom. The number of trajectories that result in a given reaction path $s$ is counted for each case, and the reaction cross section $\sigma_{s,MD}$ for that path $s$ is then determined by

$$\sigma_{s,MD} = \pi B_{max}^2 \frac{N_s}{N_T}.$$  \hspace{1cm} (1.13)

where $B_{max}$ is the maximum impact parameter and $N_T$ is the total number of trajectories that are sampled.

The non-reacting collision cross sections, $\sigma_{coll,MD}$, for each case are determined from the set of non-reacting trajectory results using the method of Tokumasu and Matsumoto [69, 70],

$$\sigma_{coll,MD} = \frac{12\sigma_{\mu,MD}}{c_r^4},$$  \hspace{1cm} (1.14)

where $\sigma_{\mu,MD}$ is the viscosity cross section, which is given as [69, 70]

$$\sigma_{\mu,MD} = \frac{1}{2N_{NR}} \sum_{i=1}^{N_{NR}} \left( \frac{c_r^4}{4} \sin^2 \chi_i + \frac{1}{3} \left( \Delta e_{int,i} \right)^2 - \frac{1}{2} \left( \Delta e_{int,i} \right)^2 \sin^2 \chi_i \right) \pi B_{max}^2,$$  \hspace{1cm} (1.15)

where $\Delta e_{int,i}$ is the change in target dimensionless molecular internal energy, normalized by $\mu c_r^2$ and $\mu$ is the reduced mass of the collision pair, $\chi_i$ is the deflection angle defined as
the change in direction of the relative velocity between the target and collider particles before and after the collision, and $N_{NR}$ is the number of non-reacting trajectories for the given case.

It follows, then, that the total cross section for each case is then the sum of the collision cross section and each of the $N_R$ reaction cross sections,

$$\sigma_{tot,MD} = \sigma_{coll,MD} + \sum_{s=1}^{N_R} \sigma_{s,MD}. \quad (1.16)$$

Total cross sections determine the collision frequency within DSMC. The MD/QCT-derived total cross sections can be tabulated and implemented directly into DSMC or, alternatively, VHS parameters (Eq. 1.1) can be determined that replicate the MD/QCT results and are easily applied in DSMC.

Post-collision internal energy values can be used to generate expected internal energy distributions or cross sections that describe internal energy relaxation processes. These tabulated results can be employed in DSMC to model inelastic collisions.

The results generated from the MD/QCT studies can be implemented into DSMC. Coupling together the collision, chemistry, and internal energy relaxation models creates a consistent, accurate approach that is mostly devoid of phenomenological assumptions or extrapolations of low-temperature data that limit the effectiveness or applicability of the baseline DSMC models.
1.4 Thesis Objective and Structure

The Ionian atmosphere and hypersonic shocks have been presented as two systems commonly modeled using the DSMC method that have relied on baseline physical models that depend on assumptions of thermal equilibrium or extrapolations of relatively low-temperature experimental data that compromise prediction accuracy. The objective of this thesis is to generate improved underlying collision, chemistry, and internal energy relaxation models for collision pairs vital to the DSMC simulations of each of these systems using the MD/QCT approach. The SO$_2$-O collision pair is studied for its importance in describing the hyperthermal interactions between the Jovian plasma torus and the upper Ionian atmosphere while the N-N$_2$ and N$_2$-N$_2$ collision pairs are studied because of their significance in hypersonic shocks. When possible, the new models will be validated by comparison to experimental data, such as dissociation rates or cross sections based on viscosity data. Further comparisons will be made to the models that are typically used in baseline DSMC simulations. The new models will be implemented into DSMC and their effect will be determined by comparing resulting predictions to those obtained using baseline methodologies.

In Chapter 2, new SO$_2$-O collision and chemistry models are developed using the MD/QCT method in order to improve Ionian atmosphere simulations. A new potential energy surface (PES) in ReaxFF [71] form is developed based on accurate \textit{ab initio} calculations. This PES is used in MD/QCT calculations to determine total collision cross sections and reaction probabilities, which are compared to pre-existing models. Then,
the new MD/QCT-generated models are employed in simple thermal nonequilibrium heat bath and 2D counterflow DSMC simulations.

In Chapter 3, the collision cross sections and reaction probabilities developed in Chapter 2 are implemented into a 1D code of the Ionian atmosphere [32]. By comparing the results with the MD/QCT-based models to those obtained using the baseline methods, an assessment on the influence of the MD/QCT methods on Ionian atmospheric predictions is made.

Chapter 4 extends the MD/QCT studies of $\text{SO}_2$-O collisions in order to model the internal energy exchange process. Distributions of post-collision $\text{SO}_2$ internal energy and post-dissociation SO internal energy are determined from the MD/QCT studies and compared to those expected using the Larsen-Borgnakke method commonly used in DSMC [57]. A strategy for utilizing the MD/QCT-generated internal energy distributions in DSMC is presented. Thermal nonequilibrium heat bath simulations with conditions similar to those observed in the upper Ionian atmosphere are used to determine the influence of the new MD/QCT-based internal energy relaxation model on DSMC simulations.

Chapter 5 focuses on the development of N-$\text{N}_2$ collision, chemistry, and internal energy relaxation models that are particularly relevant for hypersonic vehicles. Collision cross sections, reaction probabilities, and reaction rates are computed for collision conditions expected in hypersonic shocks and compared to experimentally determined values and baseline methodologies. A modified rotational relaxation collision number is computed based on a database of state-to-state cross sections. The influence of each of
these models are determined by comparing hypersonic 2D axisymmetric results to those obtained using baseline DSMC methodologies.

In Chapter 6, accurate collision, chemistry, and internal energy exchange models for the \( \text{N}_2-\text{N}_2 \) are developed using MD/QCT. A potential energy surface in ReaxFF form is fit to a large \textit{ab initio} database of MS-CASPT2 calculations from Paukku \textit{et al} [13]. Corresponding rovibrational \((v, J)\) states are determined from the PES, and a coarse-grain bin model is introduced for grouping rovibrational states together. Application of a bin model [72, 73] allows for a detailed description of the nitrogen internal energy relaxation process without the significant numerical expense of a full state-to-state description. MD/QCT-computed reaction rates are computed and compared to experimentally determined rates. The influence of the MD/QCT-based models on DSMC simulations is determined by simple thermal nonequilibrium heat bath cases. Finally, several state-specific vibrational relaxation rates are computed and compared to the popular FHO-CR [66] theoretical vibrational relaxation model.

Chapter 7 gives conclusions and discusses future work. The appendices give additional detail on MD/QCT calculations, such as the generation of initial conditions and numerical parameter sensitivities.
2.1 Introduction

In the University of Texas and Penn State DSMC studies of Io’s atmosphere referred to in Section 1.1.1, the variable hard sphere (VHS) model [4] is the baseline method for determining collision cross sections (and therefore collision frequencies) that significantly influence the general structure of the atmosphere. The baseline VHS parameters for the $\text{SO}_2$-$\text{O}^+$ and $\text{SO}_2$-$\text{O}$ collision pairs were assumed to be the average of the individual $\text{SO}_2$ and $\text{O}$ VHS parameters, and each set of parameters are based on low temperature viscosity data. Yet, the accuracy of the VHS model using these values is unknown for highly energetic collisions, such as those expected with the hypervelocity Jovian plasma torus flowing over Io at $\approx 57$ km/s [17]. Hypervelocity gases (more than $\approx 5$ times the speed of sound of air, where the speed of sound of air is $<1$ km/s) are unique because their constituent molecules are more likely to dissociate or ionize via collisions with other gas particles, may be in thermal nonequilibrium, and are difficult to replicate and observe in ground-based experiments. The total collision energy (TCE) model [4] is the baseline method for determining reaction probabilities that reliably reproduce experimental reaction rates given in modified Arrhenius form. In the TCE model, the reaction probability for collision pairs is assumed to be a function of the total collision energy.
energy [70]. However, the expected SO$_2$-atom/ion collisions in the upper atmosphere of Io are highly nonequilibrium and Arrhenius rate data based on the experimental results of Grillo [1] are for temperatures far too low (2,000 K $< T < 5,200$ K) to be suitable for hypervelocity collisions [1].

To remedy this deficiency, the previous work by Deng et al. [74, 75] sought to develop collision models based on MD/QCT techniques and modeled SO$_2$ and O collisions with a Morse-based molecular potential for the SO$_2$ molecule and a Lennard-Jones collisional interaction potential. However, in the dissociation limit, the Morse-based potential for the SO$_2$ target molecule is limited and only the SO + 2O product path was studied, neglecting, for example, the atomization process. Furthermore, since the product SO potential was modeled by the S-O Morse-pair interaction defined within the context of the SO$_2$ configuration, it over predicted the SO bond length, and thus compromised the accuracy of the reaction products and also the post-collision internal energy of the SO molecule. This effect was even more apparent when examining the O$_2$ + S + O reaction path.

Given the limitations of the previous Morse-based potential and the continuing need to develop hypervelocity collision models, two new approaches are examined in MD/QCT. First, a more accurate potential energy surface for sulfur dioxide, proposed by Murrell et al. [76] is implemented by using a multi-body polynomial expansion, such that inter-molecular forces in the dissociation limit are better resolved. Additional reaction paths are also considered, particularly the complete atomization of the SO$_2$ molecule that becomes more significant at higher collisional energies. To represent the SO$_2$-O interaction, a Lennard-Jones collisional interaction potential, mostly repulsive, was used.
However, as will be shown in the next section, the Murrell approach does not accurately predict the potential for highly compressed S-O bond lengths that are likely to occur in the hypervelocity collisions studied. Furthermore, SO$_3$ is a possible, stable configuration resulting from cold SO$_2$ + O collisions at lower energies. Under the aforementioned approach, the SO$_3$ configuration is not possible, but the ReaxFF Force field system [71] methodology allows for this possibility, and can also be trained to accurately model short S-O bond lengths. ReaxFF is a molecular dynamics simulation tool that is based on a force field allowing for continuous bond formation/breaking. The ReaxFF force field parameters are customizable to a given chemical system. As such, Density Functional Theory (DFT) [77] computations were conducted to obtain accurate single-point energy calculations of the SO$_2$ + O system, including highly compressed S-O bond lengths, and relevant daughter species. The ReaxFF force field was fit to these DFT computations to obtain a highly accurate molecular potential.

In addition to providing high-fidelity reaction cross sections for the DSMC simulations, the MD/QCT approach is also used to provide the collision cross section. Since DSMC simulates a system of binary particle collisions, the essential quantity is the collision cross section, and, as will be shown, it affects the most fundamental properties of the flow gas dynamics such as O atom penetration and shock interaction region size. The baseline collision cross section is often obtained using the Variable Hard Sphere (VHS) model of Bird [4]. In previous work [74], the VHS parameters for the SO$_2$-O species pair were assumed to be the average of the individual SO$_2$ and O VHS parameters, each of which are based on low temperature viscosity data, and clearly not designed for highly energetic collisions. Thus, the accuracy of the VHS model using these values is
unknown. We therefore use the MD/QCT approach for the two potential energy surfaces to determine total collision cross sections that are applicable to the hyperthermal gases expected in the upper atmosphere of Io.

2.2 Development of SO$_2$-O Potential Energy Surfaces

Two different approaches are considered in calculating the SO$_2$-O system potential energy, $V$, that is used to model the interatomic and intermolecular interactions in Eq. 1.11. Each of the proposed approaches are discussed in detail in this section.

2.2.1 The Murrell Potential

A potential energy surface for the sulfur dioxide target and the atomic oxygen collider was developed using the summation of a collisional interaction potential $V_{int}$ and molecular potential of the SO$_2$ molecule $V_{mol}$,

$$V = V_{mol} + V_{int},$$

where the collisional interaction potential $V_{int}$ was modeled using a Lennard-Jones 6-12 potential of the standard form,

$$V_{int} = \phi_{14}(r_{14}) + \phi_{24}(r_{24}) + \phi_{34}(r_{34})$$

$$\phi_{ij}(r_{ij}) = 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right].$$
and the pair interactions were obtained by using the combining rules [78],

\[
\sigma_{\text{SO}_2\text{O}} = \frac{1}{2} (\sigma_{\text{SO}_2} + \sigma_{\text{O}}) = 3.668 \text{Å}^2
\]  \hspace{1cm} (2.4)

\[
\varepsilon_{\text{SO}_2\text{O}} = \sqrt{\varepsilon_{\text{SO}_2} \varepsilon_{\text{O}}} = 0.345 \text{ kcal/mol}
\]  \hspace{1cm} (2.5)

The molecular potential \( V_{\text{mol}} \) was modeled using a 3-body Murrell [76] potential, defined by

\[
V_{\text{mol}} = \sum V_A^{(1)} + \sum V_{AB}^{(2)}(R_{AB}) + V_{ABC}^{(3)}(R_{AB}, R_{BC}, R_{CA}).
\]  \hspace{1cm} (2.6)

The \( \sum V_A^{(1)} \) term is the sum of the energies of adiabatically removing individual atoms from the molecular cluster, or the sum of all one-body terms. However, for this case, these terms were all set to zero in order to make the atomized system the reference energy point. The \( \sum V_{AB}^{(2)}(R_{AB}) \) term is the sum of the two-body terms, which is a function of each interatomic distance and tends to zero as \( R_{AB} \) tends to infinity, and is defined as

\[
V_{AB}^{(2)} = -D_e (1 + a_1 \rho + a_2 \rho^2 + a_3 \rho^3) \exp(-a_1 \rho),
\]  \hspace{1cm} (2.7)

\[
\rho = r_{ij} - r_{e,ij},
\]  \hspace{1cm} (2.8)

where \( D_e \) is each diatomic dissociation energy (120.2 kcal/mol for \( \text{O}_2 \) and 125.2 kcal/mol for \( \text{SO} \)), \( r_{e,ij} \) is the equilibrium bond length (1.2074 Å for \( \text{O}_2 \) and 1.4811 Å for \( \text{SO} \)), and the \( a_i \) terms are constants, each given by Murrell [76]. Lastly, the \( V_{ABC}^{(3)}(R_{AB}, R_{BC}, R_{CA}) \)
term is the three-body term dependent on the three internuclear distances. This term is based on a polynomial representation of the potential and must asymptote to zero if one of the atoms is removed to infinity. Therefore, the three-body term consists of the product of a range function $T$ and polynomial fit $P$

$$V_{ABC}^{(3)} = T_{ABC}P_{ABC}$$

(2.9)

where the range function $T$ is

$$T = \Pi[1 - \tanh(\gamma_i S_i/2)],$$

(2.10)

and the polynomial fit $P$ is

$$P = V^0 \left( 1 + \sum_i C_i \rho_i + \sum_i \sum_{i \leq j} C_{ij} \rho_i \rho_j 
+ \sum_i \sum_{i \leq j \leq k} C_{ijk} \rho_i \rho_j \rho_k 
+ \sum_i \sum_{i \leq j \leq k \leq l} C_{ijkl} \rho_i \rho_j \rho_k \rho_l \right),$$

(2.11)

and $V^0$, $C$, and $\gamma_i$ are constants and $S_i$ is the range variable, each are given by Murrell [76]. In the remainder of this chapter, the PES defined by Eq. 2.1 is referred to as the “Murrell” potential.
2.2.2 Fitting of the ReaxFF Potential

ReaxFF is a reactive force field in which the system energy $V$ is determined by the contributions from various partial energies and for binary collisions is given as [71],

$$
V = V_{\text{bond}} + V_{\text{val}} + V_{\text{pen}} + V_{\text{tors}} + V_{\text{conj}} + V_{\text{vdWaals}} + V_{\text{Coulomb}}.
$$  \hspace{1cm} (2.12)

The terms on the right-hand-side represent the contributions to the potential energy surface due to bond energies, valence angle energy contributions ($V_{\text{val}}$ and $V_{\text{pen}}$), torsion energy, conjugation effects, non-bonded van der Waals interactions, and Coulombic interactions between all atom pairs, respectively.

In order to successfully model the $\text{SO}_2 + \text{O}$ system with ReaxFF, the force field $V$ must be fit or trained to specific data points obtained from single-point energy calculations. To obtain accurate single-point energies, Density Functional Theory (DFT) computations were carried out using the Jaguar package of the Schrödinger Molecular Modeling Platform [79]. The commonly-used DFT hybrid functional B3LYP [80] was employed with the 6-311G**++ basis set [81]. This basis set is the most extensive and accurate within the Jaguar framework, with triple zeta split valence, diffuse, and polarization functions [79]. DFT minimization computations were performed for each of the ground electronic state molecular configurations possible: $\text{SO}_3(X,^1A_1')$, $\text{SO}_2(X,^1A_1)$, $\text{SO}(X,^3\Sigma^-)$, $\text{O}_2(X,^3\Sigma^-_g)$, $S(^3\text{P})$, and $O(^3\text{P})$. DFT computations were also performed on the $\text{SO}_2$ and $\text{O}$ system. This was done by calculating single-point energies for various positions of the collider $\text{O}$ around a minimized $\text{SO}_2$ structure, within the $\text{SO}_2$ plane.
In addition, single-point computations were also carried out on varying bond lengths in minimized SO\textsubscript{3}, SO\textsubscript{2}, SO, and O\textsubscript{2} molecules, and varying bond angles in SO\textsubscript{2}.

The training of the ReaxFF potential for the SO\textsubscript{2} and O system requires three basic steps. First all relevant molecular dissociation energies, single-point energies for bond lengths varying from 0.3 to 1.9 Å in SO\textsubscript{3}, SO\textsubscript{2}, SO, and O\textsubscript{2}, and single-point energies for valence angles varying from 90° to 170° in SO\textsubscript{2} are assembled into a training set. Second, weights are given to each component of the training set. In this study of hypervelocity SO\textsubscript{2} and O collisions, many of which will lead to chemical reactions, accurate prediction of dissociation is critical. Therefore, dissociation energies were given significantly more weight than bond length or valence angle contributions to the force field. Third, the set of force field parameters to be varied was specified. The SO\textsubscript{2} and O system studied called for accurate training of all O and S atomic parameters, S-O bond parameters, O-O bond parameters, O-S-O angle parameters, and S under-coordination parameters. These three steps preceded the optimization procedure, during which an initial force field was used to compute single-point energies of each component of the training set. The specified system parameters were varied to give an optimal force field in which the error of the ReaxFF-computed training set versus the provided DFT-computed values were minimized.

The pertinent dissociation energies of the studied system as computed by DFT, the trained ReaxFF potential, and the Murrell potential are given in Table 2.1. It is first observed that the ReaxFF force field, in general, agrees well with the DFT results that were used in the training, obtaining agreement to within 10%. It is noted that, in comparison to the Murrell potential, however, the ReaxFF potential predicts a much
lower SO$_2$ to SO dissociation energy, which will later be shown to be the main reaction channel. Furthermore, the ReaxFF potential predicts a much lower SO$_2$ atomization energy than the Murrell potential. Recall that the ReaxFF potential was fit not only to dissociation energies, but also to potential energies corresponding to different geometric configurations, particularly different SO$_2$-O interactions. It was found that additional accuracy in fitting the ReaxFF potential to expected dissociation energies led to poorer agreement with DFT in modeling SO$_2$-O interaction potential. Therefore, the difference between ReaxFF and the expected dissociation energies are due to the choice of weighting in the fitting routine. Table 2.2 summarizes the predicted geometry of the minimized structures of SO$_3$, SO$_2$, O$_2$, and SO as computed by DFT, the resulting ReaxFF force field, and the Murrell potential energy surface. General agreement is observed for all species geometries for the three methods.

<table>
<thead>
<tr>
<th>Process</th>
<th>Lit. Value [82]</th>
<th>DFT</th>
<th>ReaxFF</th>
<th>Murrell</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_2$+O → SO+2O</td>
<td>130.8</td>
<td>109.0</td>
<td>99.9</td>
<td>130.3</td>
</tr>
<tr>
<td>SO$_2$+O → O$_2$+S+O</td>
<td>136.4</td>
<td>104.8</td>
<td>108.5</td>
<td>135.3</td>
</tr>
<tr>
<td>SO$_2$+O → S+3O</td>
<td>254.4</td>
<td>224.9</td>
<td>224.4</td>
<td>255.5</td>
</tr>
<tr>
<td>SO$_2$+O → SO$_3$</td>
<td>81.9</td>
<td>65.4</td>
<td>67.8</td>
<td>–</td>
</tr>
<tr>
<td>SO → S + O</td>
<td>123.6</td>
<td>115.8</td>
<td>124.5</td>
<td>125.2</td>
</tr>
<tr>
<td>O$_2$ → O + O</td>
<td>118.0</td>
<td>120.0</td>
<td>115.9</td>
<td>120.2</td>
</tr>
<tr>
<td>SO$_3$ → S + 3O</td>
<td>336.3</td>
<td>290.2</td>
<td>292.1</td>
<td>–</td>
</tr>
</tbody>
</table>
Table 2.2. Summary of predicted minimized molecular geometries (bond lengths in Å, angles in degrees), as computed by DFT and resulting trained ReaxFF force field, and the Murrell potential.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Lit. Value</th>
<th>DFT</th>
<th>ReaxFF</th>
<th>Murrell</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂ S-O bond length</td>
<td>1.43[83]</td>
<td>1.46</td>
<td>1.51</td>
<td>1.43</td>
</tr>
<tr>
<td>SO₂ O-S-O angle</td>
<td>119[83]</td>
<td>118.6</td>
<td>120</td>
<td>119</td>
</tr>
<tr>
<td>O₂ bond length</td>
<td>1.21[84]</td>
<td>1.20</td>
<td>1.28</td>
<td>1.21</td>
</tr>
<tr>
<td>SO bond length</td>
<td>1.49[84]</td>
<td>1.51</td>
<td>1.53</td>
<td>1.48</td>
</tr>
<tr>
<td>SO₃ S-O bond length</td>
<td>1.43[83]</td>
<td>1.48</td>
<td>1.47</td>
<td>–</td>
</tr>
<tr>
<td>SO₃ O-S-O angle</td>
<td>120[83]</td>
<td>120</td>
<td>120</td>
<td>–</td>
</tr>
</tbody>
</table>

Figure 2.1 shows the potential energy prediction of an SO₂ molecule, holding one S-O bond length at its minimized value (see Table 2.2) and varying the other S-O bond length as determined from DFT, the ReaxFF potential, and the Murrell potential. The Murrell potential energy has a much steeper inner-wall, for S-O bond lengths less than 1.0 Å than the ReaxFF method, which was fit to the DFT data. This indicates that for collisions between SO₂ and O leading to short S-O distances, the Murrell potential will predict much higher potential energies than the ReaxFF method, and thus will be more likely to dissociate.

The potential energy footprint predicted by the Murrell [76] potential and the ReaxFF force field, is shown in Fig. 2.2. The SO₂ molecule is held in its minimized geometry, with the center of mass placed at the origin. Then, the O atom collider is moved around the minimized SO₂ structure, within its plane, and the potential energy is computed. The ReaxFF potential in Fig. 2.2(a) shows a negative energy region 1.5 Å above the sulfur atom, representing a stable formation of SO₃. The Murrell potential
Fig. 2.1. Comparison of SO$_2$ potential energy for varying S-O bond lengths, holding the other S-O bond length and the O-S-O angle at their minimized values.

form is not sufficiently general to model SO$_3$ formation, hence, this region is missing in Fig. 2.2(b). Both methods show highly repulsive behavior as the collider approaches the SO$_2$, particularly for distances less than 1 Å. Farther away from the SO$_2$ molecule, at distances greater than 4 Å from the SO$_2$ center of mass, the intermolecular potential energy is negligible. However, in general, the potential energy footprint of the ReaxFF force field is smaller than that of the Murrell potential.

Figure 2.3 shows the outer bounds of the PES region where the O collider causes the minimized SO$_2$ structure and O system to have sufficient potential energy to atomize, where the SO$_2$ is held in its minimized geometry, and the O collider is, again, in the SO$_2$ plane. In order for an atomization reaction to occur in a given SO$_2$ and O collision, the SO$_2$ molecule must have an energy above its atomization energy. For an SO$_2$ molecule
with an initial internal energy below this reaction limit, the collider O must supply the remaining energy for that reaction occur. As such, it is valuable to investigate the conditions that will lead to those energies. A collider with position inside the contour levels shown in Fig. 2.3 gives a potential energy greater than the atomization energy. It is seen in Fig. 2.3 that the target for atomization is significantly larger for the Murrell potential energy surface than the ReaxFF force field. Therefore, it is expected that the Murrell potential will predict more atomization events than the ReaxFF method.

2.3 Initial Conditions For SO$_2$ + O Collisions

Reaction and collision cross sections are required for relative collisional velocities and internal energies relevant to hypervelocity conditions of Io’s atmosphere. The initial conditions for each case are defined by the relative collision velocity and the SO$_2$ internal
Fig. 2.3. Bounding atomization energy contour for ReaxFF force field and Murrell potential, where the O collider is in the plane of a minimized SO$_2$.

energy. Relative collision velocities of 1, 2, 4, 8, 12, 16, 22, 30, 45, 60, and 80 km/s were studied. The initial SO$_2$ internal energies considered were $0.5 \times 10^{-19}$, $2.0 \times 10^{-19}$, $4.0 \times 10^{-19}$, $6.0 \times 10^{-19}$, and $8.0 \times 10^{-19}$ J. This set of initial conditions was found to sufficiently resolve the collision and reaction cross section dependency on internal energy and relative velocity. Note that the dissociation energy of SO$_2$, as seen in Table 2.1, is $6.94 \times 10^{-19}$ J (99.9 kcal/mol) using the ReaxFF potential and $9.03 \times 10^{-19}$ J (130.3 kcal/mol) for the Murrell approach. Each relative velocity and initial internal energy condition constitutes a single case. For each case, 10,000 trajectories were computed with various distributions of the SO$_2$ initial internal energy, molecular orientation, and impact parameter, defined by the SO$_2$ initial coordinates and momenta. The initial coordinates and momenta were determined through microcanonical sampling which is
reviewed in Appendix B. The maximum impact parameter selected was 5 Å, a value large enough that there were negligible interactions between SO$_2$ and O particles and to ensure that all possible collisions, even glancing blows, were considered and, with 10,000 computed trajectories, gives reaction cross section resolution of $\pi B_{\text{max}}^2/N_T = 0.007$ Å$^2$. These numerical parameters were also chosen because they were determined, through a parametric study, to lead to converged SO$_2$-O dissociation and total cross sections to within 0.1 Å$^2$.

### 2.4 Comparison of MD/QCT Cross Sections and Development of Collision Models for DSMC

#### 2.4.1 Reaction Cross Sections

Reaction cross sections are computed for each case using Eq. 1.13. The dissociation to SO and atomization reaction paths are the most dominant reaction pathways for the cases studied. The SO$_2$ + O $\rightarrow$ SO + 2O reaction path cross sections, as computed by the Murrell and ReaxFF methods for two different initial SO$_2$ internal energies are shown in Fig. 2.4. Additionally, the reaction cross section derived from the TCE model is shown, computed for initial SO$_2$ internal energy of $4.0 \times 10^{-19}$ J, using the Arrhenius parameters of Grillo et al. [1] that are given in Table 2.3. It can be seen that the Grillo-TCE reaction cross section increases much more quickly than either of the MD/QCT methods. However, the Grillo data was taken in a temperature range from 2,500-5,200 K, well below the 8 km/s and higher velocity range shown for the rapid increase in Fig. 2.4. It is therefore readily apparent that either the Murrell and ReaxFF potentials will yield
significantly different DSMC chemical models than the Grillo-TCE model. Both the
ReaxFF and Murrell reaction cross sections increase for increasing energies higher than
their dissociation energies (Table 2.1), which correspond to relative velocities of 8.1 km/s
and 9.2 km/s, respectively. The ReaxFF cross sections are higher for lower relative ve-
locities, but for very hot collisions, the Murrell cross sections are higher. Both models
show maxima, where increasing collisional velocities predict decreasing reaction cross
sections. This decreasing effect is the result of two processes. First, at higher velocities,
the probability of a collision is decreased due to the collider having less residence time
within the SO$_2$ attractive region. Therefore, colliders at higher impact parameters with
high relative velocities are more likely to pass the target without having been redirected
nearer the SO$_2$ than those moving slower. Secondly, at higher velocities, if a collision
is to occur, the probability of SO$_2$ atomization becomes more significant, as shown in
Fig. 2.5. It can be seen that the Murrell potential predicts far more than atomization
the ReaxFF model. For both reaction paths, dissociation of SO$_2$ to SO and atomization
of SO$_2$, increasing initial SO$_2$ internal energy gives higher reaction cross sections, as
expected.

| Table 2.3. Arrhenius parameters (Eq. 1.2) for SO$_2$ dissociation from Grillo et al. [1] |
|-------------------|------------------|
| $\Lambda$ [m$^3$.s$^{-1}$.molecule$^{-1}$] | $\eta$ | $E_A \times 10^{20}$ [J] |
| $2.491 \times 10^{-14}$ | 0 | 77.82 |
Fig. 2.4. Comparison of reaction cross section for $\text{SO}_2 + \text{O} \rightarrow \text{SO} + 2\text{O}$ path. A relative velocity of 8.1 km/s and 9.2 km/s corresponds to the $\text{SO}_2$ dissociation energy, for the ReaxFF and Murrell approaches, respectively.

The remaining reaction paths do not significantly contribute to the total reaction cross section,

$$\sigma_{r,\text{tot},MD} = \sum_{r=1}^{N_R} \sigma_{r,MD}$$  \hspace{1cm} (2.13)

where $N_R$ is the number of reaction channels, for either potential energy surface. For example, the $\text{SO}_2 + \text{O} \rightarrow \text{O}_2 + \text{S} + \text{O}$ reaction is an unlikely event, as shown in Table 2.4. Note that for both models, the maximum cross section for this reaction is less than 0.3 Å$^2$, giving it a probability of occurring at less than 1%. This effect is due to the fact that the O-O bond distance, in the $\text{SO}_2$ configuration, is large (about 2.5 Å) compared to its minimized bond length (1.21 Å) in the minimized $\text{O}_2$ configuration. Therefore, if the S atom is separated from the $\text{SO}_2$ molecule, only a weak attraction force between
the energetic O atoms remains and, thus, complete atomization is more likely. The reaction cross sections for the formation of SO$_3$ is also given in Table 2.4. Recall that this reaction cannot be modeled using the Murrell potential, so only the ReaxFF reaction cross sections are presented. Because the SO$_3$ molecule has a relatively low dissociation energy, its formation is rare and only occurs for very low collision energies. Even for ideal conditions, the maximum reaction probability for this reaction is less than 6%. Lastly, the SO$_2$ + O → SO + O$_2$ exchange reaction cross section is considered and tabulated in Table 2.4 only for the ReaxFF approach since this reaction also cannot be modeled with the Murrell potential. It is observed that the exchange reaction occurs for lower collisional energies and, although more prominent than the formation of SO$_3$, it is still not a dominant process. Its maximum reaction probability is less than 10%.

Fig. 2.5. Reaction cross section for SO$_2$ + O → S + 3O path
Table 2.4. $\text{SO}_2+\text{O}$ reaction cross sections for less probable channels

<table>
<thead>
<tr>
<th>Potential/Internal Energy</th>
<th>$c$ (km/s)</th>
<th>$\sigma_r$ ($\text{Å}^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{SO}_2+\text{O} \rightarrow \text{O}_2 + \text{S} + \text{O}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ReaxFF, $E_i = 0.5 \times 10^{-19}$ J</td>
<td>22</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0.00</td>
</tr>
<tr>
<td>Murrell $E_i = 0.5 \times 10^{-19}$ J</td>
<td>22</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0.26</td>
</tr>
<tr>
<td>ReaxFF, $E_i = 4.0 \times 10^{-19}$ J</td>
<td>2</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>2.33</td>
</tr>
<tr>
<td>$\text{SO}_2+\text{O} \rightarrow \text{SO}_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ReaxFF, $E_i = 4.0 \times 10^{-19}$ J</td>
<td>2</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.00</td>
</tr>
<tr>
<td>ReaxFF, $E_i = 0.5 \times 10^{-19}$ J</td>
<td>2</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>2.96</td>
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<td>2.72</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.30</td>
</tr>
<tr>
<td>$\text{SO}_2+\text{O} \rightarrow \text{SO} + \text{O}_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ReaxFF, $E_i = 0.5 \times 10^{-19}$ J</td>
<td>2</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>3.33</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>4.11</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>2.47</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.23</td>
</tr>
</tbody>
</table>
2.4.2 Total Cross Sections

The total reaction cross sections (Eq. 2.13) for all chemical channels with the Murrell potential and ReaxFF method versus relative velocity, are shown in Fig. 2.6. It is apparent that the reaction cross section increases as relative velocity increases. However, the Murrell total reaction cross section is relatively flat for relative velocities greater than that associated with the total dissociation energy, whereas the ReaxFF cross sections decrease. The higher reaction cross sections at elevated collisional velocities for the Murrell method is due to a larger force field radius, as seen in Fig. 2.2. At lower velocities, the ReaxFF potential predicts more reactive activity, as expected by its lower dissociation energies seen in Table 2.1. Lastly, at higher velocities, the reaction cross section increases with increasing initial SO\(_2\) internal energy, as expected. However, at lower velocities, the reaction cross section decreases with increasing SO\(_2\) internal energy. This is because, at these lower velocities, dissociation reactions are not possible, and SO\(_3\) formation is favored at lower collisional energies.

Figures 2.7 shows the total cross section, \(\sigma_{tot,MD}\) (defined by Eq. 1.16), and its contributing components as a function of relative collision velocity, as computed by the ReaxFF method for low initial internal energy (Fig. 2.7(a)) and high initial internal energy cases (Fig. 2.7(b)). The dominant component of the total cross section at lower velocities is the non-reacting collision cross section, as expected. However, this cross section decreases rapidly with increasing collisional velocity, whereas more reactions occur at higher energies, making the reaction cross section component more significant.
as velocity increases. This effect is more pronounced with higher initial SO\textsubscript{2} internal energy in Fig. 2.7(b), for which reactions are inherently more probable.

It is convenient to express the total cross section used in the DSMC simulations in the VHS form given in Eq. 1.1. To use the obtained Murrell and ReaxFF total cross sections in the DSMC simulations, a least-squares curve-fit to Eq. 1.1 was obtained for the internal energy of 0.5 \times 10^{-19} J cases. A summary of the VHS parameters for each curve-fit is shown in Table 2.5, with the Bird/Ozawa [4, 5] VHS data and the model from Deng [74]. The Bird/Ozawa VHS parameters for SO\textsubscript{2}-O collisions are the average of the individual SO\textsubscript{2} and O VHS parameters. The SO\textsubscript{2} VHS parameters ($d_{ref,SO_2} = 7.16 \, \text{Å}$, $\omega_{SO_2} = 0.9$) are based on low-temperature viscosity data, taken from Bird [4], and the O VHS parameters ($d_{ref,O} = 2.92 \, \text{Å}$, $\omega_O = 0.75$) are those used in prior DSMC
Fig. 2.7. Contributions to the total cross section, Eq. 1.16, as computed by the ReaxFF method for two different initial SO$_2$ internal energies. Summation of the individual reaction cross sections (solid lines) compose the total reaction cross section (blue dashed). The total cross section (black dashed) is the summation of the total reaction cross section (blue dashed) and non-reacting collision cross section defined by Eq. 1.14 (red dashed).

calculations by Deng et al. [74] and Ozawa et al [5]. The reference cross section is then given by $\sigma_{ref} = \pi d_{ref}^2$. These atomic O VHS parameters compare favorably to recent O VHS parameters based on viscosity data from Capitelli et al. [85] and Cline et al. [86]. Figure 2.8 shows the Murrell and ReaxFF total cross section results at different relative velocities, their respective fit to the VHS model, the Bird/Ozawa VHS model, and the previous results of Deng et al. [74] It can be seen that the Murrell and ReaxFF VHS total cross sections can be well fit to a VHS form and the average relative error of the computed data points to the analytic form was less than 10% over the velocity range studied.

Similar to previous work of Deng et al. [74], the ReaxFF and Murrell total cross sections are larger than the Bird/Ozawa VHS cross sections for all collision velocities, which has important implications for the DSMC simulations. At higher velocities, this difference
is mostly due to the inclusion of reaction cross sections for the Murrell and ReaxFF total cross sections. At lower velocities, the ReaxFF model predicts a much larger total cross section than the other models. This is because the ReaxFF force field, based upon DFT computations, exhibits a long-range attractive potential between the SO$_2$ and O. This feature leads to large predicted cross sections at low velocities. Lastly, because the Bird/Ozawa VHS parameters are not based upon experimental data for hypervelocity SO$_2$-O collisions, the accuracy of the VHS cross section based on these parameters is simply unknown. Comparison of the total reaction cross section curves shown in Fig. 2.7 with the Bird/Ozawa VHS cross section curve of Fig. 2.8 shows that, except for relatively low collisional velocities, the reaction probability would be unphysically greater than unity. To avoid this situation in the DSMC simulation, the reaction probability would have to be capped at unity, but this would create a statistically biased outcome for most of the hypervelocity collision space. Finally, the ReaxFF total cross section is significantly higher than the Murrell cross section for lower relative velocities, but the two approach similar values at $\approx$ 14 km/s, where their curves cross and the Murrell cross section is higher, although not significantly so.

2.5 Influence of MD/QCT Cross Sections on Counter-Flow Shock Dynamics

The reaction and total cross sections computed using the ReaxFF and Murrell potentials are implemented in the DSMC computational tool, SMILE [87]. The total cross section was fit to the VHS form, as discussed in the previous section, and reaction probabilities, i.e. the ratio of the reaction cross section to the total cross section
Fig. 2.8. Comparison of total cross sections computed by Eq. 1.16. Note that the Bird/Ozawa VHS cross section is given by Eq. 1.1 and does not include contributions from chemical reactions.

\[ \sigma_{r,MD}/\sigma_{tot,MD} \], were tabulated as a function of both relative translational energy \( E_t \) and SO\(_2\) internal energy \( E_i \) for look-up in the DSMC simulations. Because the interaction between the chemistry and collision models and the gas dynamics is complex and relatively unpredictable, zero-dimensional, time-dependent DSMC simulations are first performed to clarify the differences between the original, baseline (Grillo[1]-TCE) and new MD/QCT chemistry models. Then, an axi-symmetric counter flow of sulfur dioxide out-gassing from a 2D model of Io into the hypervelocity wind of a bombarding atomic oxygen atmosphere was modeled, representing a very simplified model of the complex planetary phenomenology modeled by Moore et al. [27, 26, 28, 29], and Walker et al. [30, 31] in full DSMC planetary simulations. The new cross sections reported here are
Table 2.5. \( \text{SO}_2\)-O species pair VHS parameters used in DSMC simulations.

<table>
<thead>
<tr>
<th>Model</th>
<th>( \sigma_{\text{ref}} , [\text{Å}^2] )</th>
<th>( \omega )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bird/Ozawa VHS</td>
<td>80.4</td>
<td>0.9</td>
</tr>
<tr>
<td>Deng(^a)</td>
<td>97.3</td>
<td>0.72</td>
</tr>
<tr>
<td>Murrell</td>
<td>69.2</td>
<td>0.616</td>
</tr>
<tr>
<td>ReaxFF</td>
<td>108.0</td>
<td>0.71</td>
</tr>
</tbody>
</table>

\(^a\)Deng et al. fitted only non-reactive MD/QCT cross-section to VHS form.

being incorporated into these detailed DSMC planetary simulations. For all simulations, internal energy exchange is modeled using the Larsen-Borgnakke method [57].

2.5.1 Thermal Nonequilibrium Heat Bath

The simulations took place in a 2 × 2 cm computational domain, with specular wall boundary conditions. Initially there are two sources of \( \text{SO}_2 \) and O computational particles with equal concentrations of \( 3.0 \times 10^{22} \) molecules/m\(^3\). Each group of particles are assumed to be described by a Maxwellian of temperature 21,570 K, which therefore implies that the significant range of velocities is between \( \sim 4 \) to 12 km/s. In this first case, only the \( \text{SO}_2 + O \rightarrow \text{SO} + 2O \) reaction is considered. The simulations are adiabatic (not isothermal), so the endothermic reaction \( \text{SO}_2 + O \rightarrow \text{SO} + 2O \) causes a decrease in temperature as a function of simulation time. The simulation was run for each of the ReaxFF, Murrell, and Grillo et al. [1] TCE models.

The resulting species number densities are shown in Fig. 2.9(a) for each model. As the dissociation reaction occurs, \( \text{SO}_2 \) number density decreases and the concentrations of O and SO increase. For most of this velocity range, the TCE reaction probability, as
shown in Fig. 2.4, is significantly higher than the ReaxFF or Murrell models. Also, the reaction probability obtained from ReaxFF is higher than the Murrell model, which has the smallest reaction cross section in this range. Therefore, the TCE model showing the fastest dissociation, and the Murrell model showing the slowest, as seen in Fig. 2.9(a), is consistent with Figs. 2.4, 2.7, and 2.8.

Fig. 2.9. 0D time-dependent DSMC Simulation results using the Murrell and ReaxFF models.

The new models developed with the Murrell and ReaxFF methods included multiple reaction paths. While the dissociation of $\text{SO}_2$ to SO is the dominant reacting process, atomization is a significant process at higher collisional energies. Therefore, a second zero-dimensional case was created, with the same conditions as previously discussed, but with an initial temperature of 1,000,000 K (corresponding to a most probable velocity
of 32 km/s), and with the atomization path enabled. Figure 2.9(b) shows that, in this case, the effects of atomization reactions are observed in the formation of atomic sulfur. There is more than twice the amount of atomic sulfur for the Murrell than the ReaxFF case at steady state. The difference between the 21,570 versus the 1,000,000 K cases is consistent with Fig. 2.5 which shows that the atomization reaction is far more likely at the higher relative velocities.

### 2.5.2 2D Counterflow

DSMC computations for a 2D counterflow model for conditions appropriate to the Io atmospheric interaction with volcanic sulfur dioxide plumes were conducted. Io is modeled as a cylinder with 60 locations of out-flowing SO$_2$ at a thermal temperature of 500 K at 10 km/s distributed evenly along the surface. Incident atmospheric O flow comes in from the left boundary at a speed of 10 km/s creating a counterflow that induces collisions between SO$_2$ and O, most of which initially occur at a relative velocity of $\approx 20$ km/s. The overall number density is $1.5 \times 10^{18}$ molecule/m$^3$.

First, to isolate the effect of the new collision model, or total cross section, all reactions were disabled. Figure 2.10 shows the spatial distribution of O mole fraction for the Murrell and ReaxFF based models compared to the baseline-Bird/Ozawa VHS model. Even without chemical reactions, the flow fields predicted by the different total collision models are significantly different. It is seen that O is less prevalent near the surface for both the ReaxFF and Murrell models compared to the Bird/Ozawa VHS cross section. This is to be expected, because as seen in Fig. 2.8, the Bird/Ozawa VHS cross section for this relative velocity (20 km/s) is significantly lower than each of the Murrell
and ReaxFF models. Therefore, with a smaller collision cross section for the Bird/Ozawa
VHS cross section, more O penetrates through the counterflow, composing more of the
atmosphere near the surface. Conversely, SO\textsubscript{2} composes less of the atmosphere near the
surface in the Bird/Ozawa VHS cross section case, as seen in Fig. 2.11. The differences
between the ReaxFF and Murrell results are not as significant, as expected, because
their collision cross sections are nearly equal for these conditions. The effect of O-
atom penetration as predicted by the Bird/Ozawa VHS versus the MD/QCT methods
is clearly observed by looking at the O streamlines, shown in Fig. 2.12. Again, there
is little difference between the streamlines for the ReaxFF and Murrell approaches, as
expected.

![Streamlines](image)

(a) Top: Bird/Ozawa VHS, Bottom: Murrell  (b) Top: Bird/Ozawa VHS, Bottom: ReaxFF

Fig. 2.10. Spatial distribution of O mole fraction from a 2D DSMC simulation of a
counterflow without chemical reactions.
Fig. 2.11. Spatial distribution of SO$_2$ mole fraction from a 2D DSMC simulation of a counterflow without chemical reactions.

Fig. 2.12. Oxygen atom streamlines for a 2D DSMC simulation of a counterflow without chemical reactions.

Next, the primary dissociation channel, SO$_2$ + O $\rightarrow$ SO + 2O reaction, was enabled, and the simulations were computed again using the same computational parameters. Figure 2.13 shows the spatial distribution of the SO mole fraction for the
Murrell and ReaxFF chemistry and collision models compared to Bird/Ozawa VHS and Grillo TCE model. The Murrell and ReaxFF models predict far less dissociation than the Bird/Ozawa VHS, Grillo TCE model, consistent with the relative dissociation rates shown in the zero-dimensional simulations. Furthermore, there is slightly more SO presence for the Murrell case compared to the ReaxFF case, as would be expected because of the higher reaction cross section for the Murrell model compared to the ReaxFF model.

Fig. 2.13. Spatial distribution of SO mole fraction from the 2D DSMC simulation of a counterflow.

Further insight for the two-dimensional counter flow simulations with the single dissociation reaction can be gleaned by studying the distribution of species along the stagnation streamline. Figure 2.14 shows a comparison of the O and SO$_2$ mole fraction profiles for the baseline Bird/Ozawa VHS, Grillo TCE model with the Murrell and
ReaxFF models. It is observed, as before, that the Bird/Ozawa VHS, Grillo TCE model allows more O penetration to the surface compared to the Murrell and ReaxFF models, which have higher total cross sections. The Murrell model has the highest total cross section, and sees the least amount of O penetration. Lastly, a look at the total species number density along the stagnation streamline shown in Fig. 2.15 illustrates the overall sensitivity of the flow structure to the chemistry and collisional model choice. It can be seen that there exist significant differences between each model both in the free stream and near the surface, illustrating how critical the proper choice of a chemistry and collisional model is.

![Graph of stagnation streamline profiles of O and SO$_2$ mole fractions for the 2D DSMC simulation of a counter flow with chemical reactions.](image)

**Fig. 2.14.** Stagnation streamline profiles of O and SO$_2$ mole fractions for the 2D DSMC simulation of a counter flow with chemical reactions.
2.6 Summary

A MD/QCT approach using the Murrell potential and ReaxFF were performed for SO$_2$ and O hypervelocity collisions for a range of initial internal energies and relative velocities relevant to atmospheric conditions on Io. It was found that the two dominant reactive processes are dissociation to SO, and atomization of the SO$_2$ molecule, particularly as relative collision velocity increases. Dissociation to O$_2$ is largely negligible, and, as found from the ReaxFF computations, SO$_3$ is formed only at very low relative velocities. Pertinent collision cross sections and reaction parameters were obtained for the SO$_2$ + O → SO + 2O reaction path for three models and was implemented into the DSMC simulations of a counter flow to study the sensitivity of the flow gas dynamics.
to chemistry models. It was observed that both the selection of both the dissociation reaction cross section and the (non-reactive) collision model have a significant effect on the counterflow, shock gas dynamic structure.

In the next chapter, the collision and chemistry models developed using the ReaxFF approach will be implemented into high-fidelity 1D simulations of the Ionian atmosphere. In Chapter 4, the ReaxFF MD/QCT results will be extended to study post-collision SO$_2$ and post-reaction SO internal energy distributions, which can be used in DSMC to improve the internal energy relaxation process in SO$_2$-O collisions.
Chapter 3

Influence of MD/QCT Chemistry Models on Simulations of the Ionian Atmosphere

3.1 Introduction

In Chapter 2, the molecular dynamics/quasi-classical trajectory (MD/QCT) method was used to numerically obtain more accurate nonequilibrium chemistry and collision models for the SO$_2$-O collision pair than those that had previously been used in DSMC simulations of the Ionian atmosphere. 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. Therefore, it is expected that simulations conducted with the MD/QCT-based collision cross section will predict less penetration of plasma torus ions into the lower Ionian atmosphere. It was also found in the MD/QCT studies that the dominant reactive process for SO$_2$-O collisions is dissociation of SO$_2$ to SO and that the MD/QCT results predicted less dissociation than the TCE model based on the low-temperature reaction rates of Grillo [1]. 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. In comparison, dissociation to O$_2$ and formation of SO$_3$ were found to be negligible processes. This has important implications for Io’s nightside and atmospheric eclipse dynamics since O$_2$ is presumably non-condensable at Io’s surface temperature [26]. In summary, it was found that the
MD/QCT studies provided quite different collision and SO$_2$ dissociation models for the hypervelocity collisions expected in the Ionian upper atmosphere compared to the baseline models, and could greatly improve the fidelity of full-scale planetary simulations. Therefore, the MD/QCT VHS parameters and reaction probabilities were implemented in the Ionian simulations of Moore et al. [27, 28], Moore [29], and Walker [32] for the SO$_2$-O collision pair in order to replace the previously used simplistic plasma heating model [22, 23, 24, 25, 26]. Those parameters were also used for the SO$_2$-O$^+$ collision pair because the O$^+$ ion effectively has the same mass as the O atom, as previously mentioned, and reliable experimental data at high temperatures does not exist for SO$_2$-O$^+$ collisions. However, the effect of these new MD/QCT-based models on Ionian planetary simulations, relative to the baseline models, has not been explicitly determined.

The objective of this chapter is to quantify the effect of replacing the baseline VHS collision and TCE chemistry models based on low temperature experimental data with those based on the MD/QCT studies with the ReaxFF PES of Chapter 2 through 1D DSMC Ionian simulations using both models.

### 3.2 Simulation Methodology

A planetary simulation DSMC code [29] is used in this study and, for simplicity, only a steady 1D atmosphere is examined. The computational domain is initially modeled as a vacuum. At the lower computational boundary, sublimation of uniform SO$_2$ surface ice at Io’s subsolar surface frost temperature of 115 K [22] populates the lower atmosphere. At the upper computational boundary, the Jovian plasma torus [17] is modeled with a cold O$^+$ ion (i.e. no thermal component) number density of 3.6
\[10^{10} \text{ m}^{-3}\] streaming radially inward toward the surface at 57 km/s. This simulated number density is an order of magnitude higher than the nominal \(O^+\) number density observed by Galileo [29] in order to promote more \(SO_2\) collisions with hyperthermal \(O\) and \(O^+\). The simplified cases do not consider photo-chemistry, magnetic-field effects, surface sputtering, or radiation. In addition, many potential gas reactions, such as \(SO_2\) recombination and \(SO\) dissociation, are not considered in order to better observe the differences between the MD/QCT and TCE chemistry models. The only reactions considered in these cases are \(SO_2\) dissociation via collisions with \(O\) and \(O^+\) (\(SO_2 + O \rightarrow SO + 2O\) and \(SO_2 + O^+ \rightarrow SO + O + O^+\)) and the atomic oxygen charge exchange reaction (\(O + O^+ \rightarrow O^+ + O\)). Therefore, atomic sulfur species, and its ions, are not modeled in this case and only \(SO_2, SO, O,\) and \(O^+\) species are considered. Note that the neglected \(S\) and \(S^+\) have been observed in energetic forms in the upper atmosphere of Io, \(S^+\) is a significant component of the plasma torus, and the masses of \(S\) and \(S^+\) are twice the masses of \(O\) and \(O^+\). Therefore, if MD/QCT models for \(SO_2-O\) and \(SO_2-O^+\) collisions have a significant effect on atmospheric predictions, it may be assumed that MD/QCT models for \(SO_2-S\) and \(SO_2-S^+\) collisions may also provide further improvement. Collisions are allowed between all considered gas species. Molecular internal energy exchange is modeled using the Larsen-Borgnakke (LB) [57] method. The simplicity of these conditions is meant to elucidate the differences in solutions obtained using MD/QCT chemistry and collision models versus those using the baseline methods. For further details about the 1D planetary simulation code, see Moore [29] and Moore et al. [27].
The computational domain is 800 km high, consisting of 400 grid points with cell sizes that resolve the smaller of the approximate local mean free path or the atmospheric scale height. Near the surface, the local mean free path is expected to be the limiting criterion for grid refinement. As such, the grid is stretched exponentially in order to keep the cell height approximately equal to or less than the local mean free path, which can be estimated from $\lambda = 1/(\sqrt{2\pi}nd^2)$. Using $d = 7.16 \times 10^{-10}$ m as the effective diameter of the dominant species, SO$_2$, and an expected number density $n$ of $\approx 9 \times 10^{16}$ m$^{-3}$ at the surface, the surface mean free path is computed to be $\approx 5$ m. As altitude increases, the number density decreases (i.e. the number density at $\approx 40$ km is over two orders of magnitude lower than at the surface), and the grid must then resolve the atmospheric scale height $H = RT/g$, where $g = 1.80$ m/s$^2$ is the Ionian gravitational constant at Io's surface. The scale height is estimated to be 8.3 km at the surface, so cell sizes at higher altitudes (greater than $\approx 40$ km) are limited to 5 km.

Many particles that cross the upper boundary at 800 km do not have escape velocity, meaning that a simple vacuum boundary is insufficient. Therefore, a large buffer cell that reduces unphysical escape is placed at the top of the domain. Particles in the buffer cell are treated as free molecular and do not undergo collisions, but are allowed to move ballistically. The top of the buffer cell is modeled as a vacuum, meaning that any particle crossing its upper boundary is deleted from the simulation. The height of the buffer cell is 1320 km, or one Io radius. Particles that hit the lower surface boundary may either stick to the surface with sticking coefficient (probability of sticking) between 0 and 1.0, or reflect diffusely. Particles that stick to the surface are deleted from the simulation. If a particle sticks and is deleted, there is no particle specifically inserted
into the simulation to replace it, but the streaming of ions from the plasma into the simulation is continuous. SO$_2$, O, and O$^+$ are modeled as condensable species with a sticking coefficient of 1.0, and SO is modeled as a semi-condensable with a sticking coefficient of 0.5.

The simulations were run for 200,000 timesteps with $\Delta t = 0.5$ s to resolve the mean time between collisions until species mole fractions, number densities, and temperatures stabilized, indicating a steady-state. The macroparameters were sampled over the final 50,000 timesteps.

Two chemistry/collision model cases are considered. The first case, henceforth referred to as the “TCE” case, is the baseline case. It uses the Bird/Ozawa\[4, 5\] VHS parameters and the TCE model based on the Grillo \[1\] Arrhenius parameters (given in Table 2.3) to determine SO$_2$ dissociation probabilities. Both models are based on relatively low-temperature experimental data. The second case, henceforth referred to as the “MD/QCT” case, uses the VHS parameters and reaction probabilities for SO$_2$ dissociation via atomic oxygen bombardment from the MD/QCT studies that utilized the ReaxFF potential of Chapter 2.

Figure 3.1 shows the VHS total cross sections used for the O-SO$_2$ and O$^+$-SO$_2$ collision pairs as a function of relative collision velocity using parameters determined from the MD/QCT VHS studies and the baseline parameters of Bird/Ozawa. The MD/QCT VHS total cross sections are more than twice the baseline Bird/Ozawa VHS cross sections for all relevant collision velocities, with differences of $\approx 30$ Å$^2$ for low relative velocities ($c_r < 10$ km/s) and a difference of $\approx 16$ Å$^2$ at the 57 km/s plasma torus velocity. It
is expected that the larger cross sections for the MD/QCT case will effectively lead to decreased penetration of the plasma torus ions into the Ionian atmosphere.

Figure 3.2 shows the dissociation probabilities for SO$_2$-O and SO$_2$-O$^+$ collisions versus relative velocity for various pre-collision SO$_2$ internal energies, $E_{i,SO_2}$, determined by the MD/QCT model and the TCE model with Grillo [1] Arrhenius parameters. It is found that the TCE probabilities are greater than unity for all SO$_2$-O or SO$_2$-O$^+$ relative velocities over 12 km/s, regardless of $E_{i,SO_2}$. However, the MD/QCT model does not show this unphysical behavior. Instead, the MD/QCT reaction probabilities approach unity with increasing relative collision energy. In these 1D simulations, many collisions occur with relative velocities greater than 12 km/s and, therefore, the TCE model will predict much more dissociation than the MD/QCT model for these energetic collisions.

The Larsen-Borgnakke method is used to model molecular internal energy exchange in the studied cases. In an inelastic collision, the Larsen-Borgnakke method samples from a Maxwell-Boltzmann distribution of internal energy at a characteristic temperature associated with the relative velocity between the colliding particles. Because the Larsen-Borgnakke method does not place a limit on post-collision molecular internal energy, collisions with sufficiently high relative velocities may result in unphysical post-collision internal energies that are much greater than the dissociation energy. Therefore, due to the highly energetic ions streaming towards the surface modeled in the studied cases, SO$_2$ molecules with $E_{i,SO_2} > D_{e,SO_2}$ are expected in the simulations. The TCE model predicts a significant probability of dissociation ($> 5\%$) for velocities between 2-4 km/s if and only if $E_{i,SO_2} > D_{e,SO_2}$, as shown by the dashed red curve compared to the dashed orange curve in Fig. 3.2. For collisions in which $E_{i,SO_2} > D_{e,SO_2}$, the MD/QCT model
uses the probabilities determined from the highest $E_{i,SO_2}$ value less than the dissociation energy used in the MD/QCT studies [88] of 3.75 eV, represented by the solid green curve in Fig. 3.2. Since the MD/QCT model has appreciable dissociation probability only for $c_r \geq 4 \text{ km/s}$, it is expected that the TCE case will predict significantly more dissociations than the MD/QCT case for collisions where $E_{i,SO_2} > D_{e,SO_2}$ and $c_r < 4 \text{ km/s}$. It is further noted that MD/QCT-determined post-collision internal energy distributions can be used to replace the Larsen-Borgnakke method for determining post-collision molecular internal energies. This new model avoids the unphysical post-collision energies that are generated by the LB method and will be explored in Chapter 4. However, these new MD/QCT-based models are not considered in the study discussed here in Chapter 3.

For both cases, the probability of an atomic oxygen resonant charge exchange reaction is modeled using the approximate cross section versus relative energy found in Smirnov [89] as outlined in detail in Moore et al [28] and Moore [29]. In a resonant charge exchange reaction, an electron is transferred between the two colliding particles with no momentum transfer. In these simulations, resonant charge exchange reactions including the high-speed incident O$^+$ ions from the plasma torus will produce fast neutral O atoms.

### 3.3 1D Simulation Results

For the chosen simulation conditions and physical parameters used in both cases, it is expected that SO$_2$ will be the dominant species at low altitudes due to the sublimating surface ice. The simplified plasma model supplements the effect of gravity in acting to compress the atmosphere, producing higher gas number densities near the surface.
Fig. 3.1. Total cross section versus relative velocity for the O-SO₂ and O⁺-SO₂ collision pairs, as determined using the VHS parameters of Bird/Ozawa (the baseline case) and those derived from the MD/QCT studies of Chapter 2.

than in the upper atmosphere [90, 26]. Additionally, the hypervelocity O⁺ ions streaming towards the surface further heat the atmosphere, initiating SO₂ dissociation. As gas temperature increases further from the surface, more SO₂ molecules dissociate and the prevalence of SO correspondingly increases. The heated atoms and molecules attain an upward velocity away from the surface. Particles with sufficient upward velocities above the exobase escape the atmosphere and replenish the plasma torus.

The gas translational temperatures for both cases are shown versus altitude in Fig. 3.3, where it can be seen that the gas temperature at low altitudes (< 10 km) approaches the 115 K surface temperature. Near the surface, temperature drops with increasing altitude in either case due to rotational and vibrational radiative cooling of
Fig. 3.2. Probability of SO$_2$ dissociation for both SO$_2$ + O → SO + 2O and SO$_2$ + O$^+$ → SO + 2O$^+$ reactions for various initial SO$_2$ internal energies, as determined from the MD/QCT method and the baseline TCE method using Grillo [1] Arrhenius parameters.

SO$_2$, with a minimum at ≈ 5 km. At these lower altitudes, there is little difference in temperature between the two models, despite the significant differences in cross sections used. This is because the system is in local thermal equilibrium at low altitudes and, therefore, the distribution of particle velocities is unaffected by changes in collision frequency. At higher altitudes, the plasma heating effects become evident with a sharp rise in temperature. However, it is observed that the MD/QCT temperature is colder than the TCE case for altitudes above ≈ 11 km. This is expected because the larger MD/QCT collision cross sections for the SO$_2$-O and SO$_2$-O$^+$ collision pairs, compared to those from the TCE case, decrease the plasma penetration into the atmosphere.
The mean bulk gas velocity and the mean species velocities for \( \text{SO}_2 \), \( \text{SO} \), and \( \text{O} \) are displayed in Fig. 3.4, where a positive velocity indicates upward movement away from the surface. Due to the plasma heating, fast neutrals attain a significant upward velocity that increases with altitude. Particles with sufficiently high velocities escape the atmosphere and act to re-supply the torus. It is noted that the upward velocity of \( \text{SO}_2 \) for the TCE model is more than twice that predicted by the MD/QCT case at altitudes above 40 km. The likelihood of an \( \text{SO}_2 \) molecule colliding with an incoming \( \text{O}^+ \) ion, which could act to slow the \( \text{SO}_2 \), is much higher for the MD/QCT case due to its larger cross section. Therefore, the heated \( \text{SO}_2 \) molecules in the TCE case are more likely to sustain higher upward velocities than in the MD/QCT case. Furthermore, because \( \text{SO}_2 \) is the dominant component of the atmosphere, this affects the upward velocity of the other constituent gas species and, therefore, the mean bulk gas velocity.

The species mole fractions with respect to altitude, regardless of altitude, are given in Fig. 3.5 for both the MD/QCT and TCE cases. Note that the gas is composed primarily of \( \text{SO}_2 \) at the surface. However, the sublimated \( \text{SO}_2 \) gas near the surface dissociates into daughter components \( \text{SO} \) and \( \text{O} \) such that the relative \( \text{SO}_2 \) content decreases as the altitude increases and the high-speed \( \text{O}^+ \) ions streaming toward the surface heat the atmosphere. However, it is noted that the MD/QCT case predicts significantly less \( \text{SO}_2 \) dissociation than the TCE case. This observation is expected, mainly due to the MD/QCT probability of dissociation being less than the TCE probability of dissociation for most high-velocity collisions [88], as shown in Fig. 3.2. The decreased \( \text{SO}_2 \) dissociation for the MD/QCT case is also due, in part, to the decreased temperatures and velocities computed in the MD/QCT case as a result of its higher collision cross
Fig. 3.3. Predictions of atmospheric gas temperature versus altitude for the MD/QCT and TCE cases.

section. It was shown in Fig. 3.2 that the probability of SO$_2$ dissociation increases with increasing relative collision velocity. Relative collision velocities tend to decrease with decreasing temperatures and mean velocities, such as those predicted by the MD/QCT case versus the TCE case. Therefore, both the updated MD/QCT chemistry and collision models lead to decreased SO$_2$ dissociation, corresponding to decreased concentrations of daughter species near the surface.

The number of SO$_2$ dissociation reactions that occurred within each 15 kilometers of altitude, $N_d(x)$, was determined for each case. This was done by first recording the altitude where each dissociation reaction occurred. Then, the 15 km bin corresponding to that altitude was incremented by 1, $N_d(x) = N_d(x) + 1$. By dividing the final $N_d(x)$ value by the total number of dissociation reactions $N_{d,total}$ in each case, the distribution
Fig. 3.4. Predictions of mean species and bulk gas velocities versus altitude for the MD/QCT and TCE cases.

of collisions leading to SO\(_2\) dissociation with respect to each 15 kilometers of altitude, \(N_d(x)/N_{d,\text{total}}\), is determined and shown in Fig. 3.6. For altitudes less than \(\approx 60\) km, it is observed that the MD/QCT case predicts a higher proportion of dissociating events than the TCE case. This is due to the lower SO\(_2\)-O collision cross section of the TCE case, which means sublimated and heated SO\(_2\) is more likely to reach higher altitudes before being impacted by the streaming ions and summarily being dissociated. The slight kink in the TCE distribution at 30-50 km altitude is believed to be an artifact associated with the grid stretching.

The distribution of collisions leading to SO\(_2\) dissociation with respect to relative collision velocity, \(N_d(c_r)/N_{d,\text{total}}\), regardless of altitude, was determined in a similar fashion to the determination of \(N_d(x)/N_{d,\text{total}}\) detailed previously, and is shown in
Fig. 3.5. Comparisons of computed mole fractions versus altitude between the MD/QCT and TCE cases.

Fig. 3.7. It is noted that a significant fraction of dissociations occur at a relative velocity of 57 km/s, \( \approx 3.5\% \) in the TCE case and \( \approx 12.5\% \) in the MD/QCT case. This is as expected because the \( O^+ \) ions are streaming down at this velocity. Furthermore, both cases predict a local distribution peak at \( \approx 10 \) km/s, a velocity that corresponds to a \( SO_2-O \) relative translational energy equal to the \( SO_2 \) dissociation energy. A greater proportion of \( SO_2 \) dissociations in the MD/QCT case occur at \( c_r = 57 \) km/s than in the TCE case. Therefore the TCE case predicts a higher proportion of dissociations to occur at lower relative velocities. In particular, the TCE method predicts a significantly higher proportion of dissociations to occur for velocities 2-4 km/s. As previously discussed and shown in Fig. 3.2, dissociations resulting from collisions with \( c_r < 4 \) km/s in the TCE case are possible only if \( E_{i,SO_2} > D_{e,SO_2} \). Furthermore, the MD/QCT dissociation
probabilities for collisions where $E_{i,SO_2} > D_{e,SO_2}$ and $c_r < 4 \text{ km/s}$ are much lower than the TCE probabilities. Therefore, the higher proportion of dissociations resulting from relative collision velocities 2-4 km/s for the TCE case indicates that there is a corresponding higher proportion of dissociations resulting from collisions with $E_{i,SO_2} > D_{e,SO_2}$. Indeed, it was found that 24% of TCE dissociations occurred for collisions with $E_{i,SO_2} > D_{e,SO_2}$, compared to only 14% for the MD/QCT case. Future DSMC Ionian simulations may consider employing a new post-collision molecular internal energy model based on MD/QCT studies [91] that will be discussed in Chapter 4. That model would prevent the production of unphysical SO$_2$ molecules where $E_{i,SO_2} > D_{e,SO_2}$.

Fig. 3.6. Distribution of dissociations with respect to altitude for the MD/QCT and TCE cases, where $N_d(x)$ is the number of dissociations that occurred at altitude $x$ and $N_{d,total}$ is the total number of dissociations computed in each case.
Fig. 3.7. Distribution of SO$_2$ dissociations with respect to relative velocity, regardless of altitude, for the MD/QCT and TCE cases, where $N_d(c_r)$ is the number of dissociations that occurred at relative velocity $c_r$ and $N_{d,total}$ is the total number of dissociations computed in each case.

The species and total number densities with respect to altitude are given in Fig. 3.8. As expected from Fig. 3.5, there is significantly more SO$_2$ throughout the domain for the MD/QCT case, which predicts far less dissociation than the TCE case. Near the surface, or for altitudes less than 20 km, there is little significant difference in bulk number density between the two models. At these low altitudes, the atmosphere is dominated by SO$_2$ from the sublimating surface frost. The maximum number density is observed at $\approx$ 5 km, corresponding to the altitude of minimum temperature shown in Fig. 3.3. It was found that the pressure decreases monotonically with increasing altitude for both cases, as expected for hydrostatic equilibrium. However, the increased number
densities of O and SO for the TCE case demonstrate the greater reactive activity near the surface. Note that photo-chemistry and electron impact dissociation of SO$_2$ were not considered in this study and each would likely significantly affect the predicted species distributions by altitude.

Lastly, the rate at which particles exit the simulation can be determined by the product of the number density, $n$, and bulk velocity, $c$, at the top of the computational domain. Because each case was in steady state (i.e. there were no temporal changes in number density) the flux through the top of the domain is assumed to be proportional to the difference between the total rate of particle generation in the computational domain (due to dissociation, sublimation of surface ice, and introduction of the plasma particles) and the total particle surface sticking rate. The MD/QCT case predicted an exit flux of
$0.83 \times 10^{15} \text{ s}^{-1}\text{m}^{-2}$, which was approximately 37\% of the exit flux of $2.24 \times 10^{15} \text{ s}^{-1}\text{m}^{-2}$ predicted by the TCE case. This difference is due primarily to the increased reactive activity and decreased total collision cross section in the TCE case. The computed exit flux does not equal the particle atmospheric escape rate, however, because a fraction of these particles leaving the domain have velocities less than the escape velocity. For both cases, the temperature at the top of the domain is $\approx 3000 \text{ K}$ and the mean flow velocity is $\approx 220 \text{ m/s}$. Assuming a Maxwellian velocity distribution at this temperature, and an escape velocity of 2.56 km/s [92], this means that only 55\% of O atoms, and less than 10\% of SO and SO$_2$ molecules, will leave the computational domain with velocities sufficient to escape the atmosphere.

### 3.4 Summary

One-dimensional DSMC simulations of Io’s atmosphere were conducted to determine the effect of implementing accurate collision and chemistry models derived from MD/QCT studies versus traditional models based on low-temperature experimental shock-tube data. It was found that the choice of collision and chemistry model had a significant effect on the atmospheric structure. Specifically, the MD/QCT case predicted approximately half the SO$_2$ dissociation due to its lower reaction probabilities, and the higher collision cross sections for the MD/QCT case led to a plasma-heating induced temperature rise further from the surface and a particle escape rate 37\% of that predicted using the baseline methodologies. Although these simple calculations did not take into account many of the physical phenomena present in the Ionian atmosphere and assumed an incident ion density one order of magnitude greater than the nominal
density, the results demonstrate the importance of using accurate collision and chemistry models in planetary simulations.
Chapter 4

An Internal Energy Model for
\( \text{O}(^3\text{P}) + \text{SO}_2(X,^1\text{A}_1) \) in DSMC
Based on Molecular Dynamics Computations

4.1 Introduction

In the Ionian DSMC simulations of Zhang et al. [25, 24, 93], Walker et al. [30, 32], and Moore et al. [27, 26, 28, 29], the continuous Larsen-Borgnakke (LB) method [57] was used to model SO\(_2\) RT energy exchange, and the discrete Bergemann and Boyd [61] method was used to model SO\(_2\) VT energy exchange, each of which are discussed briefly in Section 1.2.3. The use of the Bergemann and Boyd approach thus meant 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. [94] for temperatures ranging from 290-1090 K. Constant values of \(Z_{V,\nu_2}\) of 300 or 158 were used for gas temperatures less than or greater than 800 K, respectively and temperature-dependent \(Z_{V,\nu_1}\) and \(Z_{V,\nu_3}\) values were fit to a Millikan-White form, where \(\nu_i\) represents each of the SO\(_2\) vibrational modes. The Jovian plasma torus heating produces hyperthermal upper atmospheric temperatures above the studied range of Bass et al., as shown in Chapter 3, so the validity of using these relaxation numbers based on relatively low temperatures is unknown.

In these DSMC studies, when the product of a chemical reaction is a molecule, such as the nascent SO formed by SO\(_2\) dissociation, the reactant internal energy is
proportionally allocated to the product internal energies and the relative translational energy between the dissociated species according their respective degrees of freedom, assuming local thermal equilibrium, consistent with the LB model. While this process conserves total energy of the collision, the validity of this relatively simplistic process in determining post-reaction internal energies is unclear, particularly for the highly energetic collisions expected in the upper Ionian atmosphere.

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. Recall from the previous chapter, for example, that the LB method produced SO$_2$ internal energies above the dissociation limit, which led to unphysical reaction probabilities greater than unity. However, the upper atmosphere of Io interacts with the hypervelocity Jovian plasma torus, producing strong 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$_2$ $\nu_2$ vibrational band [95]. Due to the limitations of the commonly used DSMC models for determining post-reaction and post-collision internal energy, a new internal energy exchange model for SO$_2$-O collisions has been developed based on accurate theoretical calculations. The Molecular Dynamics/Quasi-Classical Trajectory (MD/QCT) work using the ReaxFF potential from Chapter 2 will be extended in this chapter 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.
In Chapter 2, MD/QCT studies on \( \text{SO}_2 + \text{O} \) collisions were conducted 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) \([4]\) 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 \([88]\) and a diminished gradient in the upper atmospheric temperature rise \([96]\) compared to the case using baseline VHS parameters. It was further found that the dominant reactive process for \( \text{SO}_2 - \text{O} \) collision is dissociation of \( \text{SO}_2 \) to \( \text{SO} \) 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 \([1]\). The TCE model\([4]\) is the widely used in DSMC to simulate chemical reactions between gas-phase atoms and molecules. Complete atomization of the \( \text{SO}_2 \) molecule becomes significant above relative velocities \( \approx 20 \text{ km/s} \), indicating that this reaction is likely to occur in the Ionian upper atmosphere and dissociation to \( \text{O}_2 \) and formation of \( \text{SO}_3 \) were found to be negligible processes. Finally, in similar DSMC simulations related to conditions of Io’s atmosphere in Chapter 3, it was found that the MD/QCT reaction probability predicted approximately half the \( \text{SO}_2 \) dissociation than the TCE probabilities \([88, 96]\). 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 chapter, 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 Chapter 2, 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 Chapter 2.
4.2 Methodology for Determining Post-Collision Internal Energy for Non-Reacting Trajectories

The set of SO\textsubscript{2}-O MD/QCT trajectory results employing the fitted ReaxFF potential energy surface (PES) from Chapter 2 are used to determine the resulting internal energy distributions. This means that the same set of initial collision conditions are considered that cover the range of conditions expected in the hypervelocity interactions of the upper Ionian atmosphere. The lowest initial internal energy of 1.4 kcal/mol corresponds to SO\textsubscript{2} in the ground rotational, vibrational, and electronic state. It is noted that, in this work, O is assumed to be in its ground electronic state and, therefore, the O\textsuperscript{(3P)}+SO\textsubscript{2} → O\textsuperscript{(1D)}+SO\textsubscript{2} reaction and collisions between SO\textsubscript{2} and O\textsuperscript{(1D)} are not considered. Because the relative translational energies of interest in this work (e.g. 4973 kcal/mol for a relative velocity of 57 km/s, the speed at which the Jovian plasma torus flows over Io) are significantly greater than the energy differences between the O\textsuperscript{(1D)} and O\textsuperscript{(3P)} states (45.4 kcal/mol), considering only the O\textsuperscript{(3P)} state is not expected to have a significant effect on SO\textsubscript{2} and SO post-collision internal energy distributions.

4.3 Post-Collision SO\textsubscript{2} Internal Energy Distributions for Non-Reacting Trajectories

Post-collision energies and deflection angles can be computed using the coordinates and momenta of each molecule at the end of each given trajectory computation. In the event of a dissociation reaction, post-reaction SO vibrational, rotational, and total internal energy can be computed. For non-reacting collisions, post-collision SO\textsubscript{2} internal
energy and the corresponding collider deflection angle is computed. The method used to calculate these fundamental quantities from the MD/QCT trajectory calculations is outlined below.

The total energy of a binary collision, \( E_c \), between an atom and molecule, such as those for the \( \text{SO}_2\)-O in the MD/QCT studies, is given by \( E_c = E_t + E_i \), where \( E_t \) is the translational energy, and \( E_i \) is the initial molecular internal energy. From conservation of energy, it follows that the post-collision molecular internal energy \( E'_i \) is simply \( E'_i = E_c - E'_t \). Throughout this thesis, all primes indicate that the given variable is a post-collision or post-reaction value.

The rotational energy of the molecule can be computed directly from the post-collision coordinates and momenta of its constituent atoms. The rotational energy of a given body is given by

\[
E'_{\text{rot}} = \frac{1}{2} \sum_{i=1}^{3} L_i \omega_i, \tag{4.1}
\]

where \( L_i \) and \( \omega_i \) are the angular momentum and velocity about axis \( i \), respectively. The angular momentum components \( L_i \) form the angular momentum vector \( \vec{L} \), which is determined from

\[
\vec{L} = \sum_{j=1}^{N} \vec{r}_j \times m_j \vec{c}_j, \tag{4.2}
\]

where \( j \) is the index of each atom of the molecule, and \( \vec{r}_j \) and \( \vec{c}_j \) are the atom’s position and velocity relative to the molecule center of mass, respectively. The angular momentum \( \vec{L} \) can also be defined as a function of the molecular inertia tensor \( \vec{I} \) and \( \vec{\omega} \),

\[
\vec{L} = \vec{I} \vec{\omega}, \tag{4.3}
\]
so it follows that
\[ \bar{\omega} = \tilde{I}^{-1} \tilde{L}. \] (4.4)

Having obtained \( E'_{\text{rot}} \), it follows that the post-collision vibrational energy is
\[ E'_{\text{vib}} = E'_i - E'_{\text{rot}}. \] (4.5)

Note that the rotational and vibrational energies are determined only at the end of each trajectory. However, the rotational and vibrational energies of SO\(_2\) are expected to change periodically due to changing bond lengths and the conservation of angular momentum. Because of this, the post-collision rotational and vibrational energies determined using the method described above may over-predict or under-predict rotational and vibrational energies relative to their average post-collision values. Despite this, in several sample cases in which rotational and vibrational energies were averaged over one vibrational period for each trajectory, it was found that there was relatively no effect on rotational and vibrational energy distributions compared to the distributions obtained from trajectories in which vibrational energies were computed only at the end of each trajectory. Therefore, to save computational cost in the trajectory simulations, rotational and vibrational energies are determined only at the end of each trajectory.

For polyatomic molecules such as SO\(_2\), it is interesting to study how post-collisional vibrational energy is partitioned among the modes. The vibrational modes of SO\(_2\) are: symmetric stretch (\( \nu_1 = 1151 \text{ cm}^{-1} \)), bend (\( \nu_2 = 518 \text{ cm}^{-1} \)), and asymmetric stretch (\( \nu_3 = 1361 \text{ cm}^{-1} \)). However, there is no analytic method for determining the energy in each vibrational mode with the anharmonic ReaxFF PES. Instead, the partitioning
of the vibrational energy into each of the three modes can be approximated based on a normal mode analysis approach. If the vibrational oscillations are assumed to be small, such that a simple harmonic oscillator may be assumed, and independent, a normal mode analysis of the deflections based on the PES for the SO₂ target can be carried out relative to the minimized molecular state. A post-collision molecule can then be fit to the corresponding vibrational mode using this deflection information [97],

\[ \lambda_1 \tilde{M}_1 + \lambda_2 \tilde{M}_2 + \lambda_3 \tilde{M}_3 - \tilde{D} = 0, \]  

(4.6)

where \( \tilde{M}_i \) are deflection matrices corresponding to each \( i \) vibrational mode as determined from the normal mode analysis, \( \tilde{D} \) is the MD/QCT-computed deflection matrix, and \( \lambda_i \) are numerically-determined parameters that denote how much the MD/QCT-computed deflection is due to each \( i \) vibrational mode. Because the energy stored in a simple harmonic oscillator scales with the deflection squared [97],

\[ E'_{vib} \propto k_1 \lambda_1^2 + k_2 \lambda_2^2 + k_3 \lambda_3^2, \]  

(4.7)

where \( k_i \) is the spring constant associated with each vibrational mode determined from the normal mode analysis, the vibrational energy in mode \( i \), \( E'_{vib,i} \), is

\[ E'_{vib,i} = \frac{k_i \lambda_i^2}{\sum_{j=1}^{3} k_j \lambda_j^2} E'_{vib}. \]  

(4.8)

It is noted that, for high-energy collisions, the SO₂ molecule may become highly vibrationally excited, likely violating assumptions inherent for normal mode analyses. The
energy partitions are also based on molecular deflections at the conclusion of each trajectory, rather than maximum deflections associated with each mode. As such, this method for partitioning the energy is not exact and is an approximation, but in the absence of an analytic method for determining the vibrational energy in each vibrational mode of the ReaxFF PES, it is difficult to quantify the expected numerical error associated with this approximation. Furthermore, this method for partitioning vibrational energy is determined only by the instantaneous deflections at the end of each trajectory, rather than averaging over a vibrational period. Relative to the average post-collision vibrational energy in each mode, this approach may under-predict the vibrational energy in a given mode if the instantaneous deflection is negligible but there is kinetic energy in that given mode passing through the minimized state, or it may over-predict the vibrational energy if the instantaneous deflection is at its maximum periodic deflection. However, in the several sample cases in which rotational and vibrational energies were averaged over one vibrational period for each trajectory that were referred to previously, it was also found that there was relatively no effect on the energy distributions of each vibrational mode compared to the distributions obtained from trajectories in which vibrational energies were computed only at the end of each trajectory. Moreover, it will be shown later that this methodology leads to equipartition of vibrational energy into each of the three vibrational modes, on average.
4.4 MD/QCT-Generated Internal Energy Distributions

4.4.1 SO$_2$-O Deflection Angles and Post-Collision SO$_2$ Internal Energy

The deflection angle represents the change in the collider path after collision with the target SO$_2$ and correlates strongly with changes in target SO$_2$ internal energy. A deflection angle of 180$^\circ$ indicates that the collider completely reversed its original trajectory, whereas a deflection angle of 0$^\circ$ means the collider path was unchanged. For the commonly used VHS model in DSMC, post-collision deflection angles are chosen randomly, independent of relative collision velocity and total collision energy, with $\cos(\chi) = 2R_f - 1$, where $R_f$ is a random number uniformly distributed between 0 and 1. To study the deflection angle dependence on these parameters, MD/QCT determined deflection angles were sorted into bins of 1$^\circ$ width for each case. Because the MD/QCT trajectories sampled impact parameters up to 5 Å, it was found that many trajectories did not undergo a collision and were misses with $\chi \approx 0^\circ$. To eliminate these superfluous deflection angles from the distributions, only deflection angles greater than $\approx 10^\circ$ are examined here. Figure 4.1 shows cumulative distributions of SO$_2$-O deflection angle for the VHS model and several studied MD/QCT cases. Note that the deflection angle distribution for the VHS model is independent of the VHS model parameters [4]. The cumulative distribution represents the percentage of deflection angles less than, or equal to, the given deflection angle value for non-reacting trajectories. The effect of increasing collider velocity is examined in Fig. 4.1(a) and the effect of increasing target SO$_2$ initial internal energy is shown in Fig. 4.1(b). Figure 4.1(a) shows that MD/QCT-computed deflection angle has a very strong dependence on relative velocity. In general, as relative
velocity is increased, expected deflection angle decreases. Increasing the relative velocity means increasing the momentum of the center of mass, which means more energy transfer between the two colliding particles is required in order to obtain a post-collision direction of relative velocity that corresponds to a high deflection angle. However, energy transfer in a collision is strongly dependent on the impact parameter. So, collisions with large impact parameters that may result in high deflection angles for low velocity cases give smaller deflection angles for higher velocity cases. Furthermore, collisions with small impact parameters that may lead to high deflection angles at high velocities are those that are more likely to dissociate. Figure 4.1(b) shows that increasing collisional energy by increasing target SO\(_2\) initial internal energy also tends to decrease the MD/QCT-computed deflection angle. Because the VHS model randomly selects the deflection angle, it predicts higher deflection angles than each of the MD/QCT-computed cases shown in Fig. 4.1.

As previously mentioned, there are a significant number of trajectories that are misses, for which there is no collider-target interaction, and therefore, no internal energy exchange. Inclusion of the energies from these trajectories would wrongly bias the distribution of post-collisional SO\(_2\) internal energy towards the initial internal energy. Therefore, a strategy for eliminating these misses from the MD/QCT studies was developed. As described in Section 1.3, a collision cross section \(\sigma_{\text{coll}}\) is computed for each of the collision cases presented in this paper, according to the method of Tokumasu and Matsumoto [69] (Eq. 1.14). It is assumed that the collision cross section \(\sigma_{\text{coll}}\) for each
(a) Target SO$_2$ initial internal energy: 7.2 kcal/mol

(b) Relative collision velocity: 12 km/s

Fig. 4.1. Cumulative post-collision deflection angle distributions given by MD/QCT case defined by a relative velocity and initial internal energy can also be determined by

$$\sigma_{coll} = \pi B_{\text{max}}^2 \frac{N_c}{N_T},$$  \hspace{1cm} (4.9)$$

where $B_{\text{max}}$ is the maximum impact parameter in the MD/QCT set of trajectories (5 Å in this study), $N_c$ is the number of collisions, and $N_T$ is the total number of trajectories for each case. Using the computed $\sigma_{coll}$ value from Section 2.4.2, an effective number of collisions for each case $N_c$ is determined. Then, the trajectories corresponding to the $N_c$ highest deflection angles are assumed to be collisions, and are used in determining the post-collision SO$_2$ internal energy distributions. The cut-off angle for each case is then taken as the lowest deflection angle within the set of the $N_c$ collisions.

Figure 4.2 shows the average deflection angle for all non-reacting trajectories and the
cut-off angle used to determine collisions for several of the studied cases as a function of relative velocity. It is first observed that the average deflection angle is highest for the lowest relative velocities studied. For these cases, there is significant collider-target interaction, and most trajectories result in a collision. As relative velocity increases, average deflection angle decreases, as expected. Furthermore, higher initial target SO₂ internal energy corresponds to lower average deflection angles. Collisions that result in large deflection angles correspond to large changes in target internal energy. However, as initial SO₂ internal energy increases, the allowable change in internal energy without resulting in a dissociation is limited, thus explaining the decrease in the average deflection angle and its dependence on collision energy, especially between 10 to 30 km/s.

In comparison, the VHS model predicts an average deflection angle of 90° for all cases because the deflection angle is selected randomly, independent of collision velocity or initial molecular internal energies. The cut-off deflection angle used also decreases with increasing relative velocity and initial target internal energy, and ranges between 13° and 29°.

Figure 4.3 shows cumulative post-collision SO₂ internal energy $E'_{i,SO_2}$ distributions for several studied cases. The cumulative distribution represents the percentage of post-collision SO₂ internal energy values less than, or equal to, the given energy value. The effect of increasing collider velocity is examined in Fig. 4.3(a) and the effect of increasing target SO₂ initial internal energy is shown in Fig. 4.3(b). As expected, increasing velocity means that higher post-collision energies are more probable. However, it is noted that, for all collisions, there were no post-collision energies found above the SO₂ dissociation energy of 99.9 kcal/mol. As relative velocity decreases, a collision is
increasingly likely to give a decrease in SO$_2$ internal energy. It is shown in Fig. 4.3(b) that the probability of a decrease in SO$_2$ internal energy increases with increasing initial SO$_2$ internal energy. However, as expected, post-collision internal energy increases with initial SO$_2$ internal energy.

Figure 4.4 shows the cumulative post-collision SO$_2$ vibrational energy $E'_{vib}$, rotational energy $E'_{rot}$, and internal energy $E'_i = E'_{vib} + E'_{rot}$ distributions for several cases. Figures 4.4(a) and 4.4(b) shows that increasing relative velocity, $c_r$, or $E_{i,SO_2}$ tends to increase the expected rotational and vibrational post-collision energies. In Fig. 4.4(b), it is observed that the $E_{i,SO_2} = 1.4$ kcal/mol case tends to predict more post-collision rotational energy than vibrational energy, but the $E_{i,SO_2} = 28.8$ kcal/mol case predicts...
(a) Target SO$_2$ initial internal energy: 57.6 kcal/mol

(b) Relative collision velocity: 60 km/s

Fig. 4.3. Cumulative post-collision SO$_2$ internal energy $E'_{i,SO_2}$ distributions given by MD/QCT. The dashed vertical lines in each figure represent the initial SO$_2$ internal energy value $E_{i,SO_2}$.

The opposite. Collisions that result in high rotational excitation are typically due to direct impact of the collider with one of the constituent O atoms of the SO$_2$ molecule at an angle normal to the S-O bond. These collisions are also good candidates for dissociation and as $E_{i,SO_2}$ increases, the probability of dissociation increases. Therefore, as $E_{i,SO_2}$ increases, vibrational mode excitation becomes more significant relative to the rotational mode. This effect is prominently featured in Fig. 4.5, where the average $E'_{rot}$ plateaus at approximately 8 km/s and then decreases with increasing velocity. Note that 8 km/s is a velocity that corresponds to a relative translational energy above the dissociation energy.
Figures 4.6(a) and 4.6(b) show the cumulative distribution function of post-collision energy in each vibrational mode for varying $c_r$ and $E_{i,SO_2}$, respectively. It is observed that the predicted internal energy of each mode increases with increasing collision energy. However, there is no dominant mode and the cumulative energy distributions for each vibrational mode for a given case are similar.

The average proportion of vibrational energy going into each vibrational mode ($\bar{E}_{vib,i}/\bar{E}_{vib}$ from Eq. 4.8) was determined for each computed case and found to be approximately constant across all cases: 35 ± 2%, 30 ± 2%, and 35 ± 2% for the bending, symmetric stretching, and asymmetric stretching modes, respectively. These mean MD/QCT vibrational energy partitions agree well with the high-temperature equipartition of energy assumption [97], which states that each vibrational mode contributes...
equally (33%) to the total vibrational energy. These results for hypervelocity SO$_2$-O collisions provide support to the \textit{a priori} assumption of equipartition of vibrational energy in high-temperature flows that are used in the DSMC polyatomic internal energy transfer method of Gimelshein \textit{et al} \cite{62}. Thus, on average, equipartition of vibrational energy can be assumed for the range of collision conditions studied.

To compare the MD/QCT-generated $E'_{i,SO_2}$ distributions with those predicted by the DSMC baseline LB model, the latter approach is briefly reviewed. As previously stated, the LB energy exchange model samples from an equilibrium internal energy distribution of the form\cite{59}

$$f_{E_i} \propto E_i^{\zeta_i/2-1} \exp \left(-\frac{E_i}{k_B T} \right). \quad (4.10)$$
where $E_i$, $\zeta_i$, and $T$ are the internal energy of the molecule, number of internal degrees of freedom, and the translational temperature, respectively. It is noted that this distribution function does not explicitly consider the temperature of an internal mode or the molecular bond dissociation energy as a limiter. Therefore, for collisions with sufficiently high relative velocities, such as the 57 km/s interactions between the Ionian upper atmosphere and Jupiter’s plasma torus, the expected post-collision internal energies may be unphysically well above dissociation energy when the LB method is employed.

There are several models which determine the probability that a rotationally inelastic collision, $P_r$, or vibrationally inelastic collision, $P_v$, occurs. If all collisions result in rotational and vibrational relaxation, $P_r = P_v = 1$. However, a temperature-dependent relaxation probability is typically used. In this study, $P_r(T)$ is defined by
the Parker \[63\] method, with \( T^* = 100 \) K and \( Z_{r,\infty} = 15 \) for \( \text{SO}_2 \) and \( P_v(T) \) is given from the Millikan and White \[64\] form, with characteristic \( \text{SO}_2 \) vibrational temperature \( \theta_{v,\text{SO}_2} = 5261 \) K.

Figure 4.7 compares MD/QCT cumulative \( E'_{i,\text{SO}_2} \) distributions to those obtained using the Larsen-Borgnakke method with \( P_r = P_v = 1 \) and also for temperature-dependent relaxation probabilities \( P_r(T) \) and \( P_v(T) \) at \( T = 40,000 \) K, a high temperature that may be observed in upper Ionian atmosphere interactions with the Jovian plasma torus. In these cases, the initial \( \text{SO}_2 \) internal energy \( E_{i,\text{SO}_2} = 28.8 \) kcal/mol, and in Figs. 4.7(a) and 4.7(b) a value of \( c_r = 8 \) and 16 km/s, respectively are considered. It is readily observed from Fig. 4.7 that \( E'_{i,\text{SO}_2} \) can be greater than the dissociation energy in the LB method since the maximum \( E'_{i,\text{SO}_2} \) for the LB method is limited by the total collision energy \( E_c \) in each case, 126.89 and 421.20 kcal/mol, respectively. Further, when the temperature-dependent relaxation probabilities are used, it was found that most collisions are elastic, and thus do not result in any change in \( \text{SO}_2 \) internal energy. However, a significant proportion of non-reacting inelastic hypervelocity collisions will result in unphysical \( \text{SO}_2 \) internal energies above its dissociation energy, highlighting a limitation of the existing LB methodology. Additionally, because the LB method does not place a limit on \( E'_{i,\text{SO}_2} \), it is more sensitive to relative collision velocity than the MD/QCT method.

4.4.2 Post-Reaction \( \text{SO} \) Internal Energy

If a MD/QCT trajectory results in a dissociation reaction, the post-reaction rotational, vibrational, and total internal energy \((E_{i,\text{SO}} = E_{rot} + E_{vib})\) of the product \( \text{SO} \)
Fig. 4.7. Cumulative post-collision SO$_2$ internal energy $E'_{i,SO_2}$ distributions given by MD/QCT, Larsen-Borgnakke method with $P_r = P_v = 1$, and Larsen-Borgnakke method with temperature-dependent probability of rotational and vibrational relaxation at $T = 40,000$ K.

is computed, and distributions are generated for each case. In DSMC, the TCE method of Bird [4] is typically used to model chemical reactions, which employs a version of the LB method to determine post-reaction internal energy. In that procedure, for a given collision leading to dissociation, the collision energy, $E_c$, is reduced by the energy of the reaction, $E_{rea}$, to give an intermediate collision energy $E^*_c = E_c - E_{rea}$, which proportionally decreases the SO$_2$ internal energy by $E^*_{i,SO_2} = E_{i,SO_2} (1 - E_{rea}/E_c)$. Then, in keeping with the LB model, $E^*_{i,SO_2}$ is allocated to the post-reaction SO vibrational, rotational, and SO-O translational modes proportionally with respect to the number of
degrees of freedom \( \zeta \) of each mode, \( i.e., \)

\[
E'_{\text{rot}, \text{SO}} = (\zeta_{\text{rot}, \text{SO}}/\zeta_{\text{tot}})E^*_{i, \text{SO}_2}
\]

(4.11)

\[
E'_{\text{vib}, \text{SO}} = (\zeta_{\text{vib}, \text{SO}}/\zeta_{\text{tot}})E^*_{i, \text{SO}_2}
\]

(4.12)

where \( \zeta_{\text{rot}, \text{SO}} = 2 \) and \( \zeta_{\text{vib}, \text{SO}} \) is defined by the simple harmonic oscillator approach [97] given in Eq. 1.10 and asymptotes to unity as temperature increases. Unlike the new approach for assigning post-reaction SO internal energies using MD/QCT results that will be discussed in the next section, this procedure is completely deterministic for a given collision energy, \( E_c \), and an initial internal energy \( E_{i, \text{SO}_2} \).

The average post-reaction SO internal energies as computed by MD/QCT are shown in Fig. 4.8, and compared to the post-reaction SO internal energy as determined by the LB/TCE method discussed above. It is observed that, for all collision conditions studied, the average post-reaction internal energy for the MD/QCT cases is significantly higher than the post-reaction internal energy computed by the LB method. This effect is more pronounced at lower internal energies. It is also noted that MD/QCT predicts slightly higher rotational than vibrational energy in the SO molecule.

The post-reaction SO internal energies predicted by MD/QCT for each case are sorted into bins of width 1.0 kcal/mol to examine the produced internal energy distribution. Figure 4.9 shows cumulative distributions for several studied cases, including rotational \( (E_{\text{rot}}) \), vibrational \( (E_{\text{vib}}) \), and total internal energy \( (E_i = E_{\text{rot}} + E_{\text{vib}}) \). The effect of increasing collider velocity is examined in Fig. 4.9(a) and the effect of increasing target \( \text{SO}_2 \) initial internal energy is shown in Fig. 4.9(b). First, it is noted that, consistent
with Fig. 4.8, that MD/QCT tends to predict more rotational energy than vibrational energy in the post-reaction SO. Furthermore, a small percentage of collisions that result in rotational energy above the SO dissociation energy of 124.5 kcal/mol is observed. These highly rotationally excited states are considered quasi-bound SO molecules. Conversely, no SO vibrational energies were found above the dissociation limit, as expected. Increasing the collision energy, by collision velocity or by target SO\textsubscript{2} initial internal energy, tends to increase post-reaction internal energy, as shown in Figs. 4.9(a) and 4.9(b), respectively.

![Graphs showing average internal energies](image)

(a) Target SO\textsubscript{2} initial internal energy: 7.2 kcal/mol  
(b) Target SO\textsubscript{2} initial internal energy: 28.8 kcal/mol

Fig. 4.8. Post-reaction SO internal energy obtained from the LB method and average post-reaction energies obtained from MD/QCT computations.
Fig. 4.9. Cumulative post-reaction SO rotational ($E_{rot}$), vibrational ($E_{vib}$), and total internal ($E_i$) energy distributions given by MD/QCT

4.5 Implementing MD/QCT Post-Collision Energy Distributions into DSMC

In this section, DSMC methodologies are presented for determining post-collision SO$_2$ and post-reaction SO internal energy in SO$_2$-O collisions, based on the MD/QCT energy distributions discussed in Section 4.3. In modeling DSMC collisions, the internal energy modes of SO$_2$, $E_{rot,SO_2}$ and $E_{vib,SO_2}$, the relative velocity of the SO$_2$-O pair, $c_r$, and the velocity of the center of mass $v_{cm,i}$ of the collision pair are calculated for each collision. The collision energy is then given by,

$$E_c = \frac{1}{2}m_{SO_2}c_r^2 + E_{rot,SO_2} + E_{vib,SO_2},$$

(4.13)
where the \( \text{SO}_2 \) internal energy is \( E_{i,\text{SO}_2} = E_{\text{rot,SO}_2} + E_{\text{vib,SO}_2} \).

### 4.5.1 Determination of Post-Collision \( \text{SO}_2 \) Internal Energy

The post-collision \( \text{SO}_2 \) internal energy cumulative distributions obtained from the MD/QCT studies, \( P_{\text{SO}_2}(E'_{i,\text{SO}_2}, E_{i,\text{SO}_2}, c) \), are tabulated as a function of initial conditions and for post-reaction \( E'_{i,\text{SO}_2} \). In this new procedure, post-collision \( \text{SO}_2 \) internal energy \( E'_{i,\text{SO}_2} \) is sampled from the MD/QCT distribution for internal energy. Then, internal energy is allocated to the vibrational and rotational modes proportionally according to the respective internal degrees of freedom.

1. Select a random number \( Rn \) uniformly distributed between 0 and 1.

2. Determine the corresponding post-collision \( \text{SO}_2 \) internal energy \( E'_{i,\text{SO}_2} \) such that the cumulative distribution obtained from MD/QCT, \( P_{\text{SO}_2}(E'_{i,\text{SO}_2}, E_{i,\text{SO}_2}, c_r) \), is equal to \( Rn \) by using trilinear interpolation of the tabulated values for \( E_{i,\text{SO}_2}, c_r \), and \( P_{\text{SO}_2} \).

3. Allocate \( E'_{i,\text{SO}_2} \) to internal modes proportionally according to the respective degrees of freedom, \( \zeta \):

\[
E'_{\text{vib,SO}_2} = \frac{\zeta_{\text{vib,SO}_2}}{\zeta_{\text{vib,SO}_2} + \zeta_{\text{rot,SO}_2}} E'_{i,\text{SO}_2},
\]

\[
E'_{\text{rot,SO}_2} = \frac{\zeta_{\text{rot,SO}_2}}{\zeta_{\text{vib,SO}_2} + \zeta_{\text{rot,SO}_2}} E'_{i,\text{SO}_2},
\]

where \( \zeta_{\text{rot,SO}_2} = 3 \) and \( \zeta_{\text{vib,SO}_2} \) is defined by the simple harmonic oscillator approach \[97\] given in Eq. 1.10 and asymptotes to three as temperature increases.
4. Determine post-collision relative translational energy between O and SO$_2$, $E'_{t,SO_2-O} = E_c - E'_{t,SO_2}$ and their post-collision relative velocity, $c'_{r,SO_2-O} = \sqrt{2E'_{t,SO_2-O}/\mu_{SO_2-O}}$

5. Determine final velocity of collider O and target SO$_2$ by randomly selecting directional components of relative velocity, $c'_{r,SO_2-O,i}$, using the methodology detailed in Section 11.2 of Bird [4]. The final velocities are then

$$
c'_{SO_2,j} = c_{cm,j} - c'_{r,SO_2-O,j} \frac{M_{SO_2}}{M_{SO_2} + M_O},$$
$$
c'_{O,j} = c_{cm,j} + c'_{r,SO_2-O,j} \frac{M_O}{M_{SO_2} + M_O},$$

(4.16)

where $M$ is the mass of each respective particle.

This procedure fully closes the collision problem, enforces conservation of energy, and generates a post-collision SO$_2$ energy distribution based on those obtained from MD/QCT studies. This approach does not explicitly sample from the separate MD/QCT-generated post-collision rotational and vibrational energy distributions. Instead, internal energy is allocated proportionally to each mode according to their respective degrees of freedom.

### 4.5.2 Determination of Post-Reaction SO Internal Energy

Post-reaction SO internal energy cumulative distributions $P_{SO}(E'_{t,SO}, E_{i,SO_2}, c_r)$ obtained from the MD/QCT studies are tabulated for post-reaction $E'_{t,SO}$ and pre-collision SO$_2$ internal energy and collisional relative velocity. In this new procedure, post-reaction SO internal energy is sampled from the tabulated cumulative probability
MD/QCT distributions. Then, similar to the LB method, internal energy is allocated to the vibrational and rotational modes proportionally according to the respective degrees of freedom, as shown in Eqs. 4.11 and 4.12. The difference between the new MD/QCT-based method and the LB method is, therefore, only in the determination of $E'_{i,SO}$. The following steps outline the new dissociation routine.

1. Determine $E'_{i,SO}$, $E'_{rot,SO}$, and $E'_{vib,SO}$ using the methodology of Steps 1-3 in Section 4.5.1.

2. Reduce the collision energy by the energy of the reaction, $E^*_c = E_c - E_{rea}$.

3. The total post-reaction translational energy, $E'_{t}$, is determined from conservation of energy as $E'_{t} = E^*_c - E'_{i,SO}$.

4. Define the total post-reaction relative translational energy, $E'_{t}$, as $E'_{t} = E'_{t,SO_2^*O^*} + E'_{t,SO-O}$, where $E'_{t,SO_2^*O^*}$ is the relative translational energy between the collider O and the center of mass of the dissociated SO$_2$ and $E'_{t,SO-O}$ is the relative translational energy between the daughter SO and O. Allocate $E'_{t}$ to $E'_{t,SO_2^*O^*}$ and $E'_{t,SO-O}$ according to their respective degrees of freedom,

$$E'_{t,SO_2^*O^*} = \frac{\zeta_{t,SO_2^*O^*}}{\zeta_{t,SO_2^*O^*} + \zeta_{t,SO-O}} E'_{t}, \quad (4.17)$$

$$E'_{t,SO-O} = \frac{\zeta_{t,SO-O}}{\zeta_{t,SO_2^*O^*} + \zeta_{t,SO-O}} E'_{t}, \quad (4.18)$$

where $\zeta_{t}$ is defined by Eq. 1.7.
5. Determine the velocity of the dissociated SO$_2$ center of mass, $c_{SO_2,j}^*$, and final collider O velocity, $c_{O,j}^*$, from $E'_{t,SO_2^*-O^*}$ using the methodology from Step 5 in Section 4.5.1, where $c_{r,SO_2^*-O^*}' = \sqrt{2E'_{t,SO_2^*-O^*}/\mu_{SO_2-O}}$.

6. Determine directional components of relative velocity between daughter SO and O, $c_{r,SO-O,i}'$ from $E'_{t,SO-O}$ using the methodology from Step 5 of Section 4.5.1, where $c_{r,SO-O}' = \sqrt{2E'_{t,SO-O}/\mu_{SO-O}}$.

7. Determine daughter SO and O velocities,

\[
\begin{align*}
    c_{SO,j}' &= c_{SO_2,j}^* - c_{r,SO-O,j}' \frac{M_{SO}}{M_{SO} + M_O} \\
    c_{O,j}' &= c_{SO_2,j}^* + c_{r,SO-O,j}' \frac{M_O}{M_{SO} + M_O},
\end{align*}
\]  

This procedure fully closes the dissociation problem, enforces conservation of energy, and generates a post-reaction SO energy distribution based on those obtained from MD/QCT studies.

4.6 Influence of MD/QCT-Based Energy Distributions on DSMC Simulations

The MD/QCT-based post-collision SO$_2$ and post-reaction SO internal energy models described in Section 4.5 were implemented in the DSMC computational tool, SMILE [87]. Time-dependent thermal nonequilibrium heat bath DSMC simulations were performed to examine the difference between solutions obtained using the new internal energy distributions and those obtained from the commonly used LB method.
The DSMC numerical parameters and the initialization of the thermal relaxation simulation are as follows. Total cross sections were determined using the VHS model [4] with parameters given in Table 4.1, where the VHS parameters for the SO\textsubscript{2}-O pair were those determined from Section 2.4.2 and the VHS parameters of the SO\textsubscript{2}-SO and SO-O collision pairs were taken as the average of the individual VHS parameters given in Table 4.1. The computational domain was 2 cm × 2 cm with specular wall boundary conditions. Initially there are two sources of SO\textsubscript{2} and O computational particles with equal concentrations of $3.0 \times 10^{22}$ molecules/m\textsuperscript{3}. A ratio of true to computational particles of $3 \times 10^{14}$ and a time step of $1 \times 10^{-10}$ s were used. The SO\textsubscript{2} and O computational particles are initialized by a Boltzmann distribution at a temperature of 40,000 K, a condition that means approximately 90% of SO\textsubscript{2}-O collisions occur between relative velocities of 4 and 13 km/s with an average relative velocity of 8.1 km/s. The initial SO\textsubscript{2} rotational and vibrational temperatures were sampled from a Boltzmann distribution at 1,000 K, thus giving the system a strong initial degree of thermal nonequilibrium. Since the simulations are adiabatic (not isothermal), the endothermic reaction \textit{SO\textsubscript{2} + O → SO + 2O} causes a decrease in gas translational temperature as a function of simulation time.

Table 4.1. SO\textsubscript{2}-O VHS parameters used in DSMC simulations. For all species pairs, $T_{\text{ref}} = 273$ K.

<table>
<thead>
<tr>
<th>Species or species pair</th>
<th>$d_{\text{ref}}$ [Å]</th>
<th>$\omega$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO\textsubscript{2} [4]</td>
<td>7.16</td>
<td>1.05</td>
</tr>
<tr>
<td>SO [5]</td>
<td>3.50</td>
<td>0.77</td>
</tr>
<tr>
<td>O [5]</td>
<td>2.96</td>
<td>0.75</td>
</tr>
<tr>
<td>SO\textsubscript{2}-O [88]</td>
<td>5.86</td>
<td>0.71</td>
</tr>
</tbody>
</table>
The two cases that are computed are referred to as “LB” and “MD/QCT”. In both cases, only the $\text{SO}_2 + \text{O} \rightarrow \text{SO} + 2\text{O}$ chemical reaction is modeled and the reaction probabilities are those determined from the MD/QCT results with the ReaxFF potential in Section 2.4.1. The baseline “LB” case employs the use of the LB method to determine post-collision energies for all collision pairs whereas in the case designated as “MD/QCT”, the MD/QCT-based tables are employed to determine $E'_{i,\text{SO}_2}$ for non-reacting collisions and $E_{i,\text{SO}}$ for dissociations for $\text{SO}_2$-$\text{O}$ collision pairs. In both cases, the LB method is used to determine post-collision energy for all other collision pairs ($i.e.$, $\text{SO}_2$-$\text{SO}_2$, $\text{SO}_2$-$\text{SO}$, $\text{SO}$-$\text{SO}$, and $\text{SO}$-$\text{O}$), the probability of vibrational and rotational relaxation is set to unity for all collision pairs for both cases in order to simplify the thermal relaxation process ($i.e.$ $Z_R = Z_V = 1$), and the temperature governing each internal energy exchange is a collision-based temperature. It was found that the MD/QCT case requires a relatively negligible $0.2\%$ more computational time than the TCE case.

A comparison of the resulting species mole fractions are shown in Fig. 4.10 for the MD/QCT and LB cases as a function of normalized time $\nu t$, where $\nu$ is the collision frequency $8.32 \times 10^7$ s$^{-1}$ based on the initial conditions of the heat bath. As the dissociation reaction occurs, $\text{SO}_2$ number density decreases and the concentrations of $\text{O}$ and $\text{SO}$ increase. However, it is observed that the predicted differences in species mole fraction of the bath between the MD/QCT and LB cases are quite small, especially as the simulation progresses towards steady state.
Figure 4.11 shows the predicted temperatures for the MD/QCT and LB cases. It can be seen in Fig. 4.11(a) that the SO translational, rotational, vibrational temperatures equilibrate to slightly higher values for the MD/QCT versus the LB case. This behavior is expected because, as shown in Fig. 4.8, the MD/QCT method tends to give higher average $E'_{i,SO}$ values than the LB method. Because $E'_{i,SO}$ is allocated to the vibrational and rotational modes in the same way for both the MD/QCT and LB methods, the rotational and vibrational temperature curves tend to have the same shape. Figure 4.11(b) shows the SO\textsubscript{2} translational, rotational, and vibrational temperatures for each method. Initially, for $\nu t$ up to $\approx 20$, the LB method predicts higher vibrational and rotational SO\textsubscript{2} temperatures than the MD/QCT method. As stated earlier, the average relative velocity for the SO\textsubscript{2}-O collision pair is initially 8.1 km/s. Because the LB
method gives much higher $E'_{i,SO_2}$ values than the MD/QCT method for collisions with relative velocity of $\approx 8$ km/s, as shown Fig. 4.7(a), the higher SO$_2$ internal temperatures for the LB method are expected. However, as the simulation progresses, the SO$_2$ temperatures tend to equilibrate. This is the result of increasing influence of SO$_2$-SO$_2$ and SO$_2$-SO collisions, which are modeled with the LB approach for both cases. Therefore, the increased influence of these other collision pairs tends to bring the two cases into closer agreement. The MD/QCT rotational and vibrational relaxation times are $\approx 2.2$ and $\approx 1.7$ times greater than the rotational and vibrational relaxation times given by the LB case, respectively, where the relaxation times are determined from the e-folding method as the time when $T_{rot,SO_2}/T_{tr,SO_2}$ or $T_{vib,SO_2}/T_{tr,SO_2} \geq 1 - e^{-1}$.

Fig. 4.11. 0-D time-dependent DSMC simulation temperature prediction using the MD/QCT-based internal energy model, and Larsen-Borgnakke model.

(a) SO translational, rotational, and vibrational temperatures
(b) SO$_2$ translational, rotational, and vibrational temperatures
In order to isolate the effect of the post-collisional energy distribution model, additional simulations were conducted for each case using the same conditions, but artificially only allowing SO\textsubscript{2}-O collisions. For these conditions, the MD/QCT case requires 0.3\% more computational time than the baseline LB case, which is, again, a relatively negligible difference. Figure 4.12 shows the different temperatures predicted for the MD/QCT and LB cases. Figure 4.12(a) again shows that the MD/QCT method predicts higher SO internal temperatures than the LB method. It can be seen that now the SO internal temperatures do not equilibrate with the SO translational temperature for either case because, without any further collisions, thermal relaxation does not occur. Furthermore, the differences between the LB and MD/QCT cases are greater when only SO\textsubscript{2}-O collisions are considered, as would occur in the rarefied Io environment.

Similarly, Fig. 4.12(b) shows the SO\textsubscript{2} translational, rotational, and vibrational temperatures for each case and, again, the differences in SO\textsubscript{2} internal temperature between the LB and MD/QCT cases are more pronounced when only SO\textsubscript{2}-O collisions are allowed. In particular, the MD/QCT rotational and vibrational relaxation times are $\approx 2.9$ and $\approx 2.5$ times greater than the rotational and vibrational relaxation times given by the LB case, respectively, compared to the $\approx 2.2$ and $\approx 1.7$ times differences observed when all collisions were considered in Fig. 4.11(b).

### 4.7 Summary

Post-collision SO\textsubscript{2} and post-reaction SO internal energy distributions were determined using MD/QCT for collisions between SO\textsubscript{2} and O for a range of conditions relevant to the Ionian atmosphere. It was found that the post-collisional velocities of
SO\textsubscript{2} and SO strongly depend on the collider velocity and initial SO\textsubscript{2} internal energy. In general, the expected post-collision SO\textsubscript{2} internal energy increased with increasing collision energy, but, was limited by the SO\textsubscript{2} dissociation energy. The average proportion of post-collision SO\textsubscript{2} internal energy going into vibrational energy, rather than rotational energy, increased with increasing collision energy above the SO\textsubscript{2} dissociation energy. The MD/QCT studies also showed that on average, the assumption of equipartition of energy may be assumed when allocating vibrational energy to each of the three SO\textsubscript{2} vibrational modes. The MD/QCT-generated internal energy distributions were compared to the distributions generated by the LB model, commonly used in DSMC simulations. It was found that the LB method for determining energy distributions after dissociation reactions greatly under-predicts the SO internal energy compared to MD/QCT. In addition,
the LB method for determining SO$_2$ internal energy after inelastic collisions can give unphysical SO$_2$ post-collision internal energy values, *i.e.* above the SO$_2$ dissociation limit. As such, a new post-collision internal energy model was developed for the SO$_2$-O collision pair using the distributions from the MD/QCT studies.

These models were implemented into a zero-dimensional hyperthermal relaxation DSMC simulation performed with a large initial degree of nonequilibrium between the translational and internal energy modes. When all possible collisions were considered among SO$_2$, SO, and O chemical species the new SO$_2$-O post collisional energy distribution models were not found to significantly change the equilibrium SO or SO$_2$ post collisional temperatures, but the time to equilibration took significantly longer for the MD/QCT case. Allowing inelastic collisions in the DSMC simulations for only the SO$_2$-O collision pair, however, demonstrated noticeable differences in SO and SO$_2$ internal temperatures. Therefore, new MD/QCT-generated post-collision internal energy distributions for all other molecular collision pairs are needed to fully replace the LB model and would lead to greater improvement in modeling hypervelocity internal energy exchange processes.
Chapter 5

Improved N-N₂ Collision, Chemistry, and Rotational-Translational Relaxation Models in DSMC

5.1 Introduction

The application of DSMC to hypersonic earth re-entry flows that are characterized by strong shocks was introduced in Section 1.1.2. In typical DSMC shock simulations, the N-N₂ collision pair is governed by the baseline collision, chemistry, and internal energy relaxation models detailed in Chapter 1. The collision cross section is modeled using the Variable Hard Sphere (VHS) [4] model, with parameters that are designed to replicate experimentally-determined macroscopic transport parameters. However, reliable transport data does not exist for the high-temperatures expected in the hypersonic shocks of interest in this work, so the validity of the VHS parameters commonly used for the N-N₂ is unknown. The N + N₂ → 3N dissociation reaction is usually modeled with the Total Collision Energy (TCE) approach with Park [3] Arrhenius parameters that describe the equilibrium reaction rates for relatively low temperatures. However, as will be shown later, this model significantly under-predicts the reaction rates for conditions of strong thermal nonequilibrium. Lastly, rotational-translational relaxation is typically modeled using the Larsen-Borgnakke [57] approach, where the probability of a rotationally inelastic collision is determined by the Parker model [63] for rotational relaxation number. However, it has been shown that the Parker method predicts a relatively large
rotational relaxation number for N-N$_2$ collisions at high temperatures. The consensus in the literature [98, 99, 100, 101, 102, 103] suggests that the Parker model, therefore, leads to an under-prediction of the R-T transfer rate. On the other hand, DSMC simulations employing the Parker model over-predicted the R-T transfer rate, compared to experimental shock-tube results of Fujita et al. [104], contradicting the consensus in the literature. However, as of this writing, Fujita et al. have acknowledged uncertainty in their rotational temperature measurements [105] and are re-running their test cases. In this chapter, an accurate approach to modeling N-N$_2$ interactions, including collision cross sections, reaction probabilities, and internal energy relaxation probabilities, is developed for use in DSMC in order to better simulate nonequilibrium conditions expected in a strong shock.

The aforementioned DSMC models can be significantly improved by use of the physics-based Molecular Dynamics/Quasi-Classical Trajectories (MD/QCT) approach with new accurate potential energy surfaces (PES). Jaffe et al. at NASA Ames have used the MD/QCT method to study the N($^4S_u$)-N$_2$($^1\Sigma_g^+$) system [106, 53]. The Schrödinger equation was first solved for a set of single-point nuclear configurations of the 3N system and then a PES was developed that represented the results of the electronic structure computations and correctly modeled N$_2$ dissociation. State-to-state cross sections for excitation and dissociation cross sections were determined from MD/QCT simulations performed for conditions expected in hypersonic shocks and it was found that the equilibrium dissociation rates generally agreed with experiment. The hypersonics community has started to use this database of dissociation and state-to-state rates in simple Computational Fluid Dynamics (CFD) and master equations studies.
and has used the database of corresponding cross sections to study improved nonequilibrium modeling in DSMC \cite{112, 113, 114, 115, 116}.

To make the use of this highly detailed set of state-specific rates feasible, Magin \textit{et al.} \cite{72} and Munafó \textit{et al.} \cite{73} grouped the 9399 \( \text{N}_2 \) rovibrational states defined by the Jaffe PES into a smaller number of bins and averaged the state-specific internal energy relaxation and dissociation rates within each bin. With this approach, the coarse-grain model was able to describe internal energy relaxation and dissociation processes with a reduced set of equations and offer an improvement over many existing models in 1D shock simulations. Notably, the post-shock vibrational energy level populations clearly deviated from a Maxwell-Boltzmann distribution. Furthermore, it was found that using only 20 energy bins provided converged results that agreed well with 40, 100, 200, and 500 bin models and solutions obtained using the entire state-to-state database. Kim and Boyd \cite{109} also employed the state-to-state database in 1D shock simulations and Panesi \textit{et al.} \cite{110} used it in strongly nonequilibrium heat bath master equation studies, each finding that the NASA Ames database resulted in improved dissociation and vibrational and rotational relaxation predictions.

Kim and Boyd \cite{112, 113} also employed used the state-specific cross section database in DSMC. Computations using the state-resolved model for a nonequilibrium heat bath case and a 2D flow around a cylinder case each showed improvement over previous DSMC models in modeling internal energy relaxation of nitrogen. Torres and Magin \cite{114, 115} also implemented the NASA Ames N-N\(_2\) state-specific relaxation and dissociation cross section database in simple DSMC shock computations, and found
that the state-resolved DSMC model correctly predicted pre- and post-shock equilibrium states and showed improvement over previous DSMC models.

While the Jaffe N-N\textsubscript{2} database has proven to be a valuable contribution to the hypersonics community, the computed state-to-state and dissociation cross sections had a high degree of numerical error. Furthermore, total collision cross sections were not explicitly determined, and the elastic cross sections were artificially too high due to the use of a large impact parameter. Therefore, the dataset is not ideally suited for direct use in DSMC.

The goal of this chapter is to extend the work of Jaffe et al. in order to develop accurate and consistent collision, chemistry, and rotational relaxation models specifically for use in DSMC. Using the Jaffe PES\cite{106} for the N(\textsuperscript{4}S\textsubscript{u})-N\textsubscript{2}(\textsuperscript{1}Σ\textsuperscript{+}) system, total cross sections and dissociation cross sections will be determined using MD/QCT. Additionally, a new rotational relaxation number is computed based on the Jaffe et al. database of state-to-state cross sections. The effect of implementing the MD/QCT-based models is determined through blunt body simulations with velocities ranging from 8.9 to 9.9 km/s, corresponding to Mach 18 to 25 in Sec. 5.7.

5.2 Validation of PES Implementation

In this work, the PES developed by Jaffe et al. at NASA Ames\cite{106} is used, which was previously employed to determine dissociation cross sections and rate coefficients for N\textsubscript{2}(v,J) + N \rightarrow 3N [106, 53]. This provides a unique opportunity to validate the MD/QCT code used in this study because, for similar collision conditions, MD/QCT reaction cross sections obtained in this work should agree with the results of Jaffe et al.
The $N_2(v=31, J=47) + N$ reaction was randomly selected for comparison. The vibrational energy for quantum level $v$ is modeled as a harmonic oscillator with anharmonic Morse term and the rotational energy for quantum level $J$ is modeled as a rigid-rotator with centrifugal distortion term, where each are defined as [2],

$$E_{vib} = \left(v + \frac{1}{2}\right) \omega_v \hbar c - \left(v + \frac{1}{2}\right)^2 \omega_v x_v \hbar c,$$

$$E_{rot} = J(J+1) \hbar c \tilde{B}_e - \left[J(J+1)\right]^2 \hbar c \tilde{D}_e,$$

where $h$ is Planck’s constant $(6.6261 \times 10^{-34} \text{ J-s})$, $c$ is the speed of light $(2.99792 \times 10^8 \text{ m/s})$, and the remaining parameters are defined in Table 5.1. In the MD/QCT validation trajectories, the target $N_2$ vibrational and rotational energies are pre-set to their respective values for each trajectory.

Dissociation cross sections for several relative velocities were computed and compared to those determined by Jaffe et al [106, 53]. This comparison is seen in Fig. 5.1, with the MD/QCT computed results in green, and the Jaffe et al. in red with corresponding reported error bars. It is observed that the MD/QCT computed cross sections agree, within the error reported, with the Jaffe results. Despite the significant numerical uncertainty previously in the Jaffe et al. cross sections that was previously noted, the general trends also agree between the MD/QCT and Jaffe et al. results. The large error bars in the Jaffe et al. cross sections, however, highlight the shortcomings of that particular set of results and their applicability for use in DSMC simulations that were discussed in the previous section.
Table 5.1. Spectroscopically determined properties of N$_2$ in the ground electronic state [2]

<table>
<thead>
<tr>
<th>$\omega_e$ (cm$^{-1}$)</th>
<th>$\omega_{ex}$ (cm$^{-1}$)</th>
<th>$B_e$ (cm$^{-1}$)</th>
<th>$D_e$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2359.61</td>
<td>14.456</td>
<td>2.010</td>
<td>$5.8 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

Fig. 5.1. Comparison of dissociation cross section for N$_2$(v=31,J=47) + N → 3N between the Jaffe et al. result and the MD/QCT result of this study. The agreement between the MD/QCT result and the Jaffe result validates the implementation of the Jaffe et al. PES into the MD/QCT code used in this study.

5.3 N-N$_2$ MD/QCT Initial Conditions

Each N-N$_2$ MD/QCT case in this study is defined by a relative collisional velocity $c_r$ and target N$_2$ initial internal energy $E_i$. The initial impact parameter and molecular angular orientations of each trajectory are determined from Monte Carlo sampling with
the methodology detailed in Appendix B. Trajectories with initial target internal energies up to the dissociation energy of $15.86 \times 10^{-19} J$ are desired. This enables DSMC model construction for all possible bound $N_2$ energy states in DSMC and examination of the effect of initial $N_2$ internal energy on collision and reaction cross sections. For the results shown in this chapter, vibrational and rotational energies are not explicitly specified for each case. Rather, a total target internal energy is specified, and the energy in each internal energy mode for each trajectory is sampled using the methodology detailed in Appendix B.4. The target initial internal energies studied were $E_i = 0.1, 0.5, 3.0, 6.0, 9.0, 12.0, \text{ and } 15.0 \times 10^{-19} J$, which corresponds to internal energies 0.6-94.6\% of the $N_2$ dissociation energy. Relative velocities between 0.80 and 35.91 km/s were studied, a range that covers conditions expected in hypersonic re-entry flows. A rigorous sensitivity analysis was conducted in order to determine the optimal numerical simulation parameters. A timestep of 0.05 fs was chosen such that inter-molecular forces are adequately resolved in the temporal domain, and with an initial inter-molecular distance of 10 Å chosen, 5000 timesteps per trajectory ensure that each trajectory captures all relevant collision dynamics. Lastly, it was found that a maximum impact parameter of 7 Å was large enough to include all possible collider-target interactions, yet not so large that an unnecessary number of insignificant trajectories were computed. The details of the sensitivity analysis are given in Appendix D.1.

5.4 Collision Cross Sections

Figure 5.2 shows the reaction (Eq. 1.13), non-reacting collision (Eq. 1.14), and total cross sections (Eq. 1.16) versus relative velocity for the cases where $E_i = 6.0 \times$
Recall that the total cross section is the sum of the reaction and collision cross sections. For $E_i = 6.0 \times 10^{-19}$ J, a relative velocity of 11.3 km/s gives a total collision energy equal to the N$_2$ dissociation energy. Therefore, for these cases with $E_i = 6.0 \times 10^{-19}$ J, the reaction cross section tends to increase with increasing $c_r > 11.3$ km/s. Conversely, the collision cross section decreases with increasing velocity. As collisional velocity increases, there is less time for target-collider interaction as the collider passes the target. Therefore, it becomes less likely that enough inter-molecular force will be applied between the two particles such that a collision occurs. Furthermore, “direct-hit” collisions, or those with relatively small impact parameters, are more likely to result in dissociations as relative velocity increases. Thus, the total cross section decreases with increasing velocity.

Figure 5.3 shows the total cross section versus relative velocity for the N-N$_2$ collision pair. The symbols represent the MD/QCT results, which exhibit the common power-law relationship with respect to velocity and relatively little dependence on $E_i$, allowing for the MD/QCT results to be fit to the commonly used VHS form, represented by the black curve. A measure of the quality of a least-squares curve fit is the coefficient of determination $R^2$, with value ranges from 0.0 to 1.0, where a value of 1.0 indicates that the model fits the data well. The MD/QCT VHS fit was found to have an $R^2$ value of 0.974. The MD/QCT curve agrees reasonably well with the Bird [4]/Ozawa [5] and Svehla [6]/Stallcop [7] curves, which are each taken as the average of the individual N$_2$ and N VHS parameters. The MD/QCT fit, Bird/Ozawa, and Svehla/Stallcop VHS parameters are given in Tbl. 5.2. Note that the Svehla/Stallcop VHS parameters are based on higher temperature (up to 10,000 K) viscosity data than the Bird/Ozawa
Fig. 5.2. MD/QCT-computed collision, reaction, and total cross sections versus relative velocity for the N-N\textsubscript{2} pair with \(E_i = 6.0 \times 10^{-19}\) J.

parameters (273 K). Later, the Bird/Ozawa VHS parameters will be taken as the baseline in DSMC simulations in Section 5.7 when examining the effect of the new MD/QCT-derived total cross section on hypersonic flowfield predictions.

5.5 Reaction Probabilities and Comparison of Reaction Rates to Experiment

Figure 5.4 shows the MD/QCT results for reaction probability, compared to the commonly used TCE model \[4\] with the Park \[3\] Arrhenius coefficients listed in Table 5.3 and compared to the QK model \[8\] with \(\theta_v = 3371\) K for \text{N}_2. The MD/QCT reaction probabilities tend to asymptote to unity as collision energy increases, whether
Fig. 5.3. MD/QCT-computed total cross sections for the N-N$_2$ pair for various initial internal energies. The MD/QCT results fit to the VHS form of Eq. 1.1 are compared to established VHS curves for the N-N$_2$ pair using Bird [4]/Ozawa [5] and Svehla [6]/Stallcop [7] VHS parameters.

by increasing initial N$_2$ internal energy or the relative collision velocity. In order for a dissociation reaction to occur, the total energy of the collision must be above the dissociation energy of the molecule. Recall that the N$_2$ dissociation energy $D_e = 15.86 \times 10^{-19}$ J. This corresponds to a relative velocity of $c_r = \sqrt{2D_e/\mu_{N-N_2}} = 14.3$ km/s. As such, for the lowest $E_i$ case (red curve), dissociation only occurs for $c_r > 14.3$ km/s. As the initial N$_2$ internal energy increases, the collision velocity needed to give a total collision energy above the dissociation energy decreases, allowing for dissociation at lower velocities. It is noted that the TCE method shows unphysical behavior in failing to predict increasing reaction probabilities as collision energy is increased. The MD/QCT probabilities are, in general, lower than the TCE model for relative velocities up to $\approx$
Table 5.2. VHS parameters for N-N\textsubscript{2} collisions.

<table>
<thead>
<tr>
<th>Model</th>
<th>Species</th>
<th>$\omega$</th>
<th>$d_{reff} \text{ [Å]}$</th>
<th>$T_{reff} \text{ [K]}$</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>MD/QCT VHS Fit</td>
<td>N-N\textsubscript{2}</td>
<td>0.725</td>
<td>3.768</td>
<td>1000</td>
<td>-</td>
</tr>
<tr>
<td>Bird/Ozawa</td>
<td>N</td>
<td>0.75</td>
<td>2.96</td>
<td>273</td>
<td>Ozawa [5]</td>
</tr>
<tr>
<td></td>
<td>N\textsubscript{2}</td>
<td>0.74</td>
<td>4.11</td>
<td>273</td>
<td>Bird [4]</td>
</tr>
<tr>
<td></td>
<td>N-N\textsubscript{2}</td>
<td>0.745</td>
<td>3.535</td>
<td>273</td>
<td>*</td>
</tr>
<tr>
<td>Svehla/Stallcop</td>
<td>N</td>
<td>0.65</td>
<td>3.11</td>
<td>1000</td>
<td>Svehla [6]</td>
</tr>
<tr>
<td></td>
<td>N\textsubscript{2}</td>
<td>0.68</td>
<td>3.58</td>
<td>1000</td>
<td>Stallcop [7]</td>
</tr>
<tr>
<td></td>
<td>N-N\textsubscript{2}</td>
<td>0.665</td>
<td>3.345</td>
<td>1000</td>
<td>*</td>
</tr>
</tbody>
</table>

*: The N-N\textsubscript{2} VHS parameters are taken as the average of the respective individual N and N\textsubscript{2} VHS parameters.

18 km/s, and both the MD/QCT and TCE probabilities are lower than those predicted from the QK model. However, for excited N\textsubscript{2} molecules with high internal energies, the MD/QCT model tends to predict higher dissociation probabilities than the TCE model. The MD/QCT dissociation probabilities for each case, $P_{r,MD}(c_r, E_i)$, will be tabulated and used in DSMC, and ensuing results will be compared to those determined using the baseline TCE model in Section 5.7.1.

The reaction probabilities determined by MD/QCT are a significant departure from those obtained using the TCE method. The computed MD/QCT probabilities are intended for hyperthermal flow conditions for which reliable experimental data does not exist. Therefore, a rigorous validation of the MD/QCT probabilities for these conditions is not possible. However, experimentally determined equilibrium dissociation rates can be compared with those determined from the MD/QCT cross sections. The reaction
Table 5.3. Arrhenius parameters (Eq. 1.2) for nitrogen dissociation from Park [3]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$A \text{ [m}^3\text{s}^{-1}\text{-molecule}^{-1}]$</th>
<th>$\eta$</th>
<th>$E_A \text{ [J]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N + N_2 \rightarrow 3N$</td>
<td>$4.981 \times 10^{-8}$</td>
<td>-1.6</td>
<td>$15.63 \times 10^{-19}$</td>
</tr>
<tr>
<td>$N_2 + N_2 \rightarrow N_2 + 2N$</td>
<td>$1.162 \times 10^{-8}$</td>
<td>-1.6</td>
<td>$15.63 \times 10^{-19}$</td>
</tr>
</tbody>
</table>

Fig. 5.4. $N + N_2 \rightarrow 3N$ reaction probabilities for various initial $N_2$ internal energies $E_i$ computed by the MD/QCT and compared to those obtained from the TCE method [4] using Park Arrhenius parameters [3] and those obtained from the QK model [8].

The rate is determined by,

$$k_r(T) = \int_0^\infty \int_0^\infty f(E_i)f(c_r)\sigma_r(c_r, E_i)c_r dE_i dc_r, \quad (5.3)$$
where \( f(E_i) \) is the continuous distribution function for internal energy,

\[
f(E_i) = \frac{E_i^{\zeta_i/2-1}}{\Gamma(\zeta_i/2)(k_B T)^{\zeta_i/2}} \exp\left(-\frac{E_i}{k_B T}\right),
\]

(5.4)

where \( \zeta_i \) is the number of internal degrees of freedom, and \( f(c_r) \) is the distribution function for relative velocity,

\[
f(c_r) = \frac{4\mu^{3/2} c_r^2}{\pi^{1/2}(2k_B T)^{3/2}} \exp\left(-\frac{\mu c_r^2}{2k_B T}\right).
\]

(5.5)

Figure 5.5 shows the computed dissociation reaction rates for the MD/QCT results compared to the shock tube data of Hanson [10] (valid for \( 5,700 < T < 12,000 \) K), Appleton [9] (\( 8,000 \) K \( < T < 15,000 \) K), Byron [11] (\( 6,000 \) K \( < T < 9,000 \) K), and Cary (\( 6,000 \) K \( < T < 10,000 \) K). The equilibrium reaction rate computed from the MD/QCT results in the solid black curve agrees well with the established shock tube data, giving a measure of validation for the MD/QCT method for these conditions. The spread in the experimental reaction rates also demonstrates in the inherent uncertainty in determining high temperature reaction rates. The QK model [8] equilibrium reaction rate is also shown to qualitatively agree with the experimental data, although it predicts more dissociation than the MD/QCT rates.

The Park Two-Temperature model [3] is commonly used in CFD in order to determine nonequilibrium reaction rates as a function of translational temperature, \( T \), and vibrational temperature, \( T_v \). A modification is made to the Arrhenius form given
by Eq. 1.2 to account for a temperature controlling the reaction, $T_a = \sqrt{TT_v}$,

$$k(T, T_v) = \Lambda T^\eta \exp \left(-\frac{E_A}{k_B T_a}\right).$$

(5.6)

Figure 5.6 compares MD/QCT-computed reaction rates to those obtained using the Park two-temperature model [3] for thermal equilibrium with internal temperature $T_i = T$ and thermal nonequilibrium with $T_i = 1000$ K and $T_i = 5000$ K. In the computation of the MD/QCT nonequilibrium rates, it is assumed that $T_i = T_v = T_r$. It is first observed that the MD/QCT thermal equilibrium rate in the solid black curve agrees well to the Park model thermal equilibrium rate in the dashed black curve, as expected, because the Park model uses Arrhenius parameters (listed in Table 5.3) that are curve-fit to the experimental values shown in Fig. 5.5. However, when the internal temperatures are set to 5000 K, the MD/QCT method predicts reaction rates approximately 1 order of magnitude greater than the phenomenological Park model for $10,000/T < 1$. When the internal temperatures are set to 1000 K, thus giving stronger thermal nonequilibrium for high temperatures, the MD/QCT model then predicts reaction rates several orders of magnitude greater than the Park model. These findings agree with those of Magin et al. [107], where strong thermal nonequilibrium dissociation rates computed from the Jaffe et al. [53] database and the analytic dissociation model of Macheret and Adamovich [117] were also both several orders of magnitude greater than the Park model. This indicates that the Park model is not well-suited to determine reaction rates for highly nonequilibrium flows.
Fig. 5.5. N + N\textsubscript{2} → 3N thermal equilibrium reaction rates computed from the MD/QCT method compared to the shock-tube data of Appleton [9], Hanson [10], Byron [11], and Cary [12]. Experimental reaction rates are shown only for the relevant temperature range used in each study. The reaction rates for the QK model [8] are also shown.

5.6 Development of a New Rotational Relaxation Number

As discussed in Section 5.1, the Parker et al. [63] model predicts a large rotational relaxation number for N-N\textsubscript{2} collisions that leads to under-prediction of the R-T transfer rate. The Parker method gives an expression for \( Z^C_R(T) \) for continuum methods

\[
Z^C_R(T) = \frac{Z_{r,\infty}}{1 + \frac{\pi^3}{2} \left( \frac{T^*}{T} \right)^{1/2} + \left( \frac{\pi^2}{4} + \pi \right) \frac{T^*}{T}},
\]  

(5.7)
Fig. 5.6. $N + N_2 \to 3N$ reaction rates computed from the MD/QCT method for thermal equilibrium ($T_i = T$), and thermal nonequilibrium ($T_i = 1000$ K and $T_i = 5000$ K) compared to the rates obtained using the Park two-temperature model [3].

where $Z_{r,\infty}$ and $T^*$ are constants. For the case of $N_2$, $Z_{r,\infty} = 18.5$ and $T^* = 91$ K are used. For use in DSMC, the following correction is made to $Z_R(T)$

$$Z_R = \frac{\zeta_t}{\zeta_t + \zeta_{rot}} Z_C,$$

(5.8)

where $\zeta_t$ and $\zeta_{rot}$ are the translational and rotational degrees of freedom, respectively [118]. An improvement on this model is desired through the use of MD/QCT results.

The Jaffe database [53] provides state-specific $N-N_2$ cross sections given for relative translational energy $E_t$ (where $E_t = \mu c_r^2/2$, $\mu$ is the reduced mass of the $N-N_2$ pair, and $c_r$ is the relative velocity), initial rotational and vibrational states $J$ and $v$ and final states $J'$, $v'$, $\sigma(E_t, J, v, J', v')$. Some $N-N_2$ trajectories result in an exchange reaction,
a process defined by \( N_1 + N_2 N^3 (J, v) \rightarrow N^3 + N_1 M^2 (J', v') \) and the cross sections for such processes are also included in the set of \( \sigma(E_t, J, v, J', v') \) cross sections.

In the computation of non-equilibrium flows in DSMC, accurate rotational-translational (R-T) relaxation is critical for numerical prediction quality. Directly using the state-specific cross sections of the Jaffe database would be ideal, yet would significantly add to overall computation time. A simpler approach would be to strategically bin the cross sections to effectively give a smaller set of cross sections to handle, however this still significantly introduces additional computation time. Simpler still, however, would be to compute an effective temperature-dependent rotational collision number \( Z_{R,\text{eff}}(T) \) from the Jaffe database. The following presents a new methodology for computing \( Z_{R,\text{eff}}(T) \).

The rotational collision number is defined as

\[
Z_{R,\text{eff}}(T) = \frac{\sigma_{\text{el}}(T) + \sigma_{\text{rot}}(T)}{\sigma_{\text{rot}}(T)},
\]  

where \( \sigma_{\text{el}}(T) \) and \( \sigma_{\text{rot}}(T) \) are thermally averaged elastic and rotational relaxation cross sections, respectively, each to be determined from the Jaffe state-to-state cross section database.

There are 9399 possible \((v,J)\) levels of \( N_2 \) in the ground electronic state, with \( J_{\text{max}} = 279 \) and \( v_{\text{max}} = 60 \), thus giving \( 9399^2 \) possible state-to-state cross sections for each of 39 relative velocities studied, not including dissociation cross sections. For simplicity, only the ground vibrational state is initially considered in the computation of
That is,
\[ \sigma(E_t, J, J') = \sigma(E_t, J, v = 0, J', v' = 0). \] (5.10)

It follows, then, that the elastic and rotational relaxation cross sections as a function of \( E_t \) and \( J \) are

\[ \sigma_{el}(E_t, J) = \sigma(E_t, J, J' = J) \]
\[ \sigma_{rot}(E_t, J) = \sum_{J' \neq J} \sigma(E_t, J, J') \] (5.11)

In order to obtain \( \sigma_{el}(T) \) and \( \sigma_{rot}(T) \), the cross sections are successively thermally averaged at temperature \( T \) over the initial rotational states \( J \), and then over translational energy \( E_t \), according to the method of Raff and Porter [68]. First, intermediate cross sections \( \sigma^*_{el}(T, E_t) \) and \( \sigma^*_{rot}(T, E_t) \) are determined by thermally averaging over initial rotational state \( J \) by,

\[ \sigma^*_{el}(T, E_t) = Q_{rot}^{-1} \sum_{J=0}^{J_{max}} \Delta J (2J + 1) \exp \left( \frac{-E_{rot,J}}{k_B T} \right) \sigma_{el}(E_t, J) \] (5.12)
\[ \sigma^*_{rot}(T, E_t) = Q_{rot}^{-1} \sum_{J=0}^{J_{max}} \Delta J (2J + 1) \exp \left( \frac{-E_{rot,J}}{k_B T} \right) \sigma_{rot}(E_t, J), \]

where \( \Delta J \) is the rotational level spacing between reported values in the Jaffe database and \( Q_{rot} \) is the rotational partition function

\[ Q_{rot} = \frac{8\pi^2 \mu^2 k_B T}{h^2} \] (5.13)
where $\mu = 1.5506 \times 10^{-26}$ kg is the reduced mass of the N-N$_2$ collision pair, the bond length $r_e = 1.094$ Å, and $h$ is Planck’s constant. The N$_2$ rotational energy $E_{\text{rot},J}$ is evaluated using the rigid-rotor with centrifugal distortion form [2]

$$E_{\text{rot},J} = J(J+1)hc\tilde{B}_e - [J(J+1)]^2hc\tilde{D}_e, \quad (5.14)$$

where rotational constants $\tilde{B}_e$ and $\tilde{D}_e$ are given by Karplus and Porter [2] are are listed in Table 5.1.

Finally, the intermediate cross sections are then thermally averaged over the translational energy $E_t$,

$$\sigma_{el}(T) = Q_t^{-1} \sum_{E_t=E_{t,\text{min}}}^{E_{t,\text{max}}} \Delta E_t \exp \left( \frac{-E_t}{k_BT} \right) \sigma_{el}^*(T, E_t), \quad (5.15)$$

$$\sigma_{rot}(T) = Q_t^{-1} \sum_{E_t=E_{t,\text{min}}}^{E_{t,\text{max}}} \Delta E_t \exp \left( \frac{-E_t}{k_BT} \right) \sigma_{rot}^*(T, E_t),$$

where $Q_t$ is the translational energy partition function

$$Q_t = \frac{8\mu^{1/2}E_t}{\pi^{1/2}(2k_BT)^{3/2}}. \quad (5.16)$$

Therefore, $Z_{R,\text{eff}}(T)$ can be computed according to Eq. 5.9 using the cross sections from Eq. 5.15. This value is plotted for temperatures ranging from 1,000-20,000 K and compared to the commonly used temperature-dependent Parker model [63] in Fig. 5.7. Additionally, the $Z_{R,\text{eff}}(T)$ is computed for $v = v' = 10$ and $v = v' = 20$. It is first observed that the computed $Z_{R,\text{eff}}$ values are significantly less than those predicted.
by the empirical Parker method. Furthermore, it is observed that the effective rotational relaxation collision number is approximately 2.5 for the range of temperatures studied in the ground vibrational state. However, as $v$ increases, there is increasing dependence on $T$, yet $Z_{R, eff}(T)$ is still limited to the range of 1.8-3.5 for the temperatures studied. Therefore, in the DSMC studies of this work, a constant $Z_R = 2.5$ is used and compared to the Parker model.

![Graph](image)

**Fig. 5.7.** Effective rotational relaxation collision number determined from the Jaffe MD/QCT database for $N + N_2$ collisions
Table 5.4. Free Stream Conditions for DSMC Simulations\(^a\) of hypersonic flow around the Aeroassist Flight Experiment (AFE) vehicle geometry.

<table>
<thead>
<tr>
<th>Altitude [km]</th>
<th>(n_\infty) [m(^{-3})]</th>
<th>(T_\infty) [K]</th>
<th>Speed [m/s]</th>
<th>(K_{n,\infty}) ((L=0.01) m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>78</td>
<td>(5.81 \times 10^{20})</td>
<td>197.0</td>
<td>8910</td>
<td>(8.95 \times 10^{-4})</td>
</tr>
<tr>
<td>90</td>
<td>(6.56 \times 10^{19})</td>
<td>188.0</td>
<td>9890</td>
<td>(7.84 \times 10^{-3})</td>
</tr>
</tbody>
</table>

\(^a\)Free stream consists of 100% \(N_2\).

5.7 Numerical Flow Modeling Technique in DSMC

The influence of the MD/QCT-based collision, chemistry, and rotational relaxation models will be evaluated in the context of DSMC simulations of 8.9 and 9.9 km/s flows around the Aeroassist Flight Experiment (AFE) vehicle geometry with a constant wall temperature of 500 K at the altitudes of 78 and 90 km, respectively. The free-stream flow conditions were taken from the Aeroassist Flight Experiment (AFE) test cases [52], and are listed in Table 5.4. The elliptically blunted cone forebody has a 2.3 m nose radius and 60° half-angle. With an assumed 0° angle of attack, the flow is modeled as axisymmetric. Again, the SMILE [87] DSMC computational tool is used. The simulations employed \(\approx 600,000\) simulated particles, 60,000 collisional cells, and 60,000 macro-parameter cells. The time step was \(2 \times 10^{-7}\) s and the macro-parameter sampling was performed with 39,000 steps after 1,000 pre-sampling steps.

Ionization and excited electronic states are not considered, and the free-stream consists of 100% \(N_2\). Therefore, only the N and \(N_2\) species in their electronic ground
states are possible in these cases. Two dissociation reactions are included in the simulations, \( \text{N}_2 + \text{N}_2 \rightarrow \text{N}_2 + 2\text{N} \) and \( \text{N}_2 + \text{N} \rightarrow 3\text{N} \). The second reaction rate is typically five to 100 times higher than the first, because relative velocities and collision frequencies between two \( \text{N}_2 \) molecules are generally lower than for the \( \text{N}-\text{N}_2 \) pair. In this chapter, the choice of the MD/QCT or TCE reaction probability for only the second reaction is studied. For the first reaction, reaction probabilities are determined using the TCE model with the Park [3] Arrhenius parameters listed in Table 5.3.

In these high speed cases, the strong shocks will significantly heat the gases surrounding the vehicle structure, which leads to complex flowfields with thermal and chemical nonequilibrium. The effects of each of the thermochemical nonequilibrium models are expected to be strongly coupled to one another, which means that implementing all of the new models at once would make it prohibitively difficult to determine the relative effect of each of the new models. Therefore, the effect of each of the new models are determined separately by comparing results to those obtained using the baseline models.

### 5.7.1 \( \text{N}_2 \) Dissociation in the Shock Layer

First, the effect of the MD/QCT-based \( \text{N}-\text{N}_2 \) dissociation reaction model is determined by comparing its simulation results to those obtained using the baseline TCE [4] model with Park [3] Arrhenius parameters. The only difference between each case is the reaction model as both cases use the baseline Svehla/Stallcop cross section and Parker rotational relaxation number.

Figure 5.8 shows the stagnation line temperatures, number densities, and mole fractions for the 78 km, 8.9 km/s case as determined from each of the \( \text{N} + \text{N}_2 \rightarrow 3\text{N} \)
reaction models. The translational temperature for the TCE case peaks at \( \approx 36,000 \) K and is greater than 25,000 K for approximately \(-0.55 \text{ m} < X < -0.2 \text{ m}\), whereas the temperature for the MD/QCT case peaks at \( \approx 32,000 \) K and is greater than 25,000 K only for approximately \(-0.45 \text{ m} < X < -0.34 \text{ m}\), as seen in Figs. 5.8(a) and 5.8(b), respectively. The decreased temperature for the MD/QCT case is caused by the increase in \( \text{N}_2 \) dissociation, seen in Figs. 5.8(c) and 5.8(d). At the stagnation point, \( \text{N}_2 \) comprises only 30\% of the gas for the MD/QCT case compared to 54\% for the TCE case. Due to the energy loss by the dissociation reactions, the shock width is reduced for the MD/QCT case. It is noted that the vibrational and rotational temperatures for both cases are well above 15,000 K within most of the shock, which indicates that the constituent \( \text{N}_2 \) molecule internal energies are significantly excited. As seen in Fig. 5.4, the MD/QCT dissociation probabilities for excited \( \text{N}_2 \) molecules are typically greater than those determined from the TCE model, which therefore explains the increased reactive activity for the MD/QCT case. Lastly, the reaction model did not have a significant effect on the predicted rotational and vibrational nonequilibrium.

Figure 5.9 shows the stagnation line temperatures, number densities, and mole fractions for the 90 km, 9.9 km/s case as determined from each of the \( \text{N} + \text{N}_2 \rightarrow 3\text{N} \) reaction models. It is first noted that this condition leads to significantly higher translational temperatures and a corresponding increase in \( \text{N}_2 \) dissociation compared to the 78 km, 8.9 km/s condition, as expected. However, the effect of the reaction model on the simulation results for these high-altitude conditions are relatively the same as those determined for the previous lower-altitude conditions. The translational temperature for the TCE case peaks at \( \approx 50,000 \) K, whereas the temperature for the MD/QCT case
peaks at \( \approx 32,000 \) K, as seen in Figs. 5.9(a) and 5.9(b), respectively. The decreased temperature for the MD/QCT case is again caused by the increase in \( \text{N}_2 \) dissociation, seen in Figs. 5.8(c) and 5.8(d). There is only 28\% \( \text{N}_2 \) at the stagnation point in the
MD/QCT case, compared to 46% for the TCE case. The shock width is again reduced for the MD/QCT case due to the additional energy lost in the dissociation process.

Fig. 5.9. Stagnation line temperatures and number densities (top subfigures (a) and (b)) and mole fractions (bottom subfigures (c) and (d)) for the 90 km, 9.9 km/s case as determined by simulations using each of the studied $N+N_2\rightarrow 3N$ reaction models.
5.7.2 Importance of the Total Cross Section

Next, the sensitivity of the flowfield to the N-N\textsubscript{2} total collision cross section is explored for both free-stream conditions. Results obtained using the baseline N-N\textsubscript{2} Bird/Ozawa VHS parameters are compared to those obtained using the fitted MD/QCT VHS parameters. The VHS parameters for each model are listed in Table 5.2. To elucidate the effect of the N-N\textsubscript{2} total cross section, the free stream mole fractions are artificially set to 50% N and 50% N\textsubscript{2}. The simulations consider no chemical reactions and use the baseline Parker model to determine the rotational relaxation number. Figure 5.10 shows the number density and translational/vibrational temperatures along the stagnation line for both free stream conditions. As shown in Fig. 5.3, the VHS cross sections derived from MD/QCT using the Jaffe PES are generally higher than those given by the baseline Bird/Ozawa VHS parameters. These higher cross sections result in increased collision frequencies between the N and N\textsubscript{2} species, which further causes a narrower shock profile compared to the baseline case. The influence of the total cross section on the shocklayer is important at both altitudes and is readily observable in the translational temperature and number density profiles. While the total cross section has a significant effect on the shock structure, the maximum translational temperatures predicted by each total cross section are relatively unchanged. The maximum temperatures predicted using each cross section model agree to within 2% for both flow conditions. Furthermore, the cross section model does not appear to have a significant effect on the relative degree of thermal nonequilibrium within the shock.
Fig. 5.10. Stagnation line number densities and temperatures for the 78 km and 90 km flowfield conditions as determined by simulations using each of the studied total cross section models. The “NewVHS” results refer to those obtained using the MD/QCT-derived N-N$_2$ total cross section.

5.7.3 Sensitivity to Rotational Relaxation

Lastly, the effect of the N$_2$ rotational relaxation number is explored for the 90 km condition. Two cases are computed, one with the baseline temperature-dependent Parker model and the other with the MD/QCT-derived constant $Z_R = 2.5$. Both cases employ
the TCE dissociation model and the baseline Bird/Ozawa VHS parameters for the total cross section. Results obtained using the baseline model are compared to those obtained using the MD/QCT-derived constant $Z_R = 2.5$ in Fig. 5.11, which shows stagnation line number density, translational and internal temperatures, and mole fractions. Recall, from Figure 5.7, that the Parker model generally over-predicts the rotational relaxation collision number for high temperatures, meaning that the rotational-translational transfer rate for those temperatures is too low. This leads to relatively low rotational temperatures within the shock. The maximum computed rotational temperature for the Parker case is only 14,000 K, compared to the maximum rotational temperature of 21,000 K for the MD/QCT case. Because the MD/QCT case gives more energy to the rotational mode, this causes a corresponding decrease in translational temperature. The MD/QCT maximum translational temperature is approximately 4% less than that predicted by the baseline Parker case.

5.8 Summary

The Molecular Dynamics/Quasi-Classical Trajectory (MD/QCT) method was used with the Jaffe et al. PES to develop accurate and consistent collision, chemistry, and rotational-translational energy relaxation models for the N-N$_2$ collision pair, specifically for use in DSMC simulations of hypersonic shocks. The MD/QCT-derived total cross sections were fit to the commonly used VHS form and agreed well with the established baseline VHS parameters for N-N$_2$ collisions, but were slightly greater than the cross sections determined using the baseline Bird/Ozawa VHS parameters. The MD/QCT N$_2$ dissociation probabilities were much more dependent on initial N$_2$ internal energy
Fig. 5.11. Stagnation line temperatures and number densities (top subfigures (a) and (b)) and mole fractions (bottom subfigures (c) and (d)) for the 90 km, 9.9 km/s case as determined by simulations using each of the studied rotational relaxation number models.

and relative velocity than the baseline TCE model with Park Arrhenius parameters. For collisions with sufficient energy to dissociate N$_2$, the MD/QCT dissociation probabilities tended towards unity with increasing collision energy, whereas the TCE probabilities
show unphysical behavior in decreasing with increasing collision energy. Lastly, a constant rotational relaxation number of $Z_R = 2.5$ was derived from the Jaffe et al. set of state-to-state cross sections and was significantly lower than the $Z_R$ predicted by the temperature-dependent Parker model, which had previously been shown to under-predict the rotational-translational relaxation rate in strong hypersonic shocks.

The new MD/QCT-derived collision, chemistry, and rotational collision numbers were implemented into 2D axisymmetric hypersonic flows over the Aeroassist Flight Experiment (AFE) geometry. The effect of each new MD/QCT-based model was distinct and significant. The total cross sections led to narrower shock profiles, the dissociation probabilities gave increased $N_2$ dissociation and a corresponding decrease in translational temperature, and the constant $Z_R = 2.5$ produced higher rotational temperatures.
Chapter 6

Modeling of Molecular Nitrogen Collisions, Internal Energy Relaxation, and Dissociation Processes for DSMC

6.1 Introduction

In Chapter 5, the motivation for generating accurate and consistent MD/QCT-based DSMC collision, chemistry, and internal energy relaxation models for the N-N$_2$ pair was presented in the context of improving hypersonic flowfield simulations. Similarly, it follows that the N$_2$-N$_2$ molecular pair must also be accurately modeled. The shortfalls of the baseline N$_2$-N$_2$ DSMC models are the same as those discussed for the N-N$_2$ pair in Section 5.1 and, as such, the N$_2$-N$_2$ models can also be improved through the use of the MD/QCT approach.

Jaffe et al. [14] extended their N-N$_2$ MD/QCT studies to examine N$_2$(1$\Sigma^+_g$)-N$_2$(1$\Sigma^+_g$) dissociation and internal energy transfer. Due to the infeasibility of computing and tabulating state-to-state rate coefficients for all $\approx 10^{15}$ possible combinations of initial and final rovibrational state pairs, cross sections and rates were determined using a coarse-grained bin model, similar to the bin models for the N-N$_2$ collision pair developed by Magin et al. [72] and Munafó et al. [73] discussed in Section 5.1. The computed equilibrium dissociation rates were found to agree well with relatively low-temperature experimental data. However, to date, the Jaffe et al. N$_2$-N$_2$ dissociation and internal
energy relaxation rates, cross sections and corresponding potential energy surface used in their MD/QCT studies are not publicly available.

A recently developed, highly advanced and publicly available \textit{ab initio} dataset has been developed for the $\text{N}_2(1\Sigma^+_g)\text{-N}_2(1\Sigma^+_g)$ pair by Paukku \textit{et al.} [13] that can be used to develop new N$_2$-N$_2$ potential energy surfaces [13, 119]. Therefore, in this chapter, a new N$_2$-N$_2$ PES is developed using the ReaxFF [71] molecular dynamics tool based on these electronic structure calculations in Section 6.2. Corresponding rovibrational $(v,J)$ levels are determined and a methodology for grouping rovibrational states into internal energy bins is presented. The use of the ReaxFF-fitted potential and bin model in MD/QCT is then described in Section 6.3, and resulting dissociation and internal energy excitation rates are shown in Section 6.4, where the dissociation rates are compared to experiment and existing dissociation models. The generation of DSMC $\text{N}_2$-$\text{N}_2$ reaction, collision, and internal energy exchange models based on the MD/QCT calculations is given in Section 6.5. The influence of the new MD/QCT-based $\text{N}_2$-$\text{N}_2$ DSMC models, coupled with the new N-N$_2$ models developed in Chapter 5 are explored in a thermal nonequilibrium heat bath. Finally, in Section 6.7, state-specific vibrational relaxation rates are computed and compared to the increasingly popular FHO-CR [15] model that was discussed in Section 1.2.3.
6.2 The ReaxFF Fitted N$_2$-N$_2$ Potential Energy Surface

6.2.1 Development of the Potential Energy Surface

A new PES in a ReaxFF [71] form was developed for the N$_2$-N$_2$ system based on the recent \textit{ab initio} dataset of Paukku \textit{et al.} [13], consisting of over 11,000 MS-CASPT2 single-point energy values in the electronic ground state, distributed along nine series of N$_2$ + N$_2$ geometries defined by the coordinates $r_a$, $r_b$, $d$, $\theta_a$, $\theta_b$, and $\phi$ shown in Fig. 6.1 and three series of N$_3$ + N geometries. The general procedure for training a ReaxFF potential energy surface (PES) was detailed in Section 2.2.2.

![Fig. 6.1](image)

Fig. 6.1. Coordinates for the N$_2$-N$_2$ system. The figure is a variation of Figure 1 in Paukku \textit{et al.} [13].

The MS-CASPT2 results [13] were used as the training set for the 4N system. In the fitting process, additional weight was given to dissociation energies and N$_2$-N$_2$ interactions expected to be significant in MD/QCT trajectories, and less weight was
given to those MS-CASPT2 results that predict very high energies that will rarely be observed. The ReaxFF fitting process consists of sequentially varying the parameters contributing to Eq. 2.12 in order to obtain an optimized set of parameters in which the weighted sum of differences between the ReaxFF-computed potential energies and the corresponding \textit{ab initio} results in the training set is minimized.

Figure 6.2(a) shows the derived ReaxFF potential and corresponding \textit{ab initio} MS-CASPT2 calculations of the 4N system versus varying bond length $r_b$ for various intermolecular distances $d$, where $r_a = 1.098$ Å, $\theta_a = \theta_b = 90^\circ$, and $\phi = 0^\circ$, effectively showing the dissociation of a single N$_2$ molecule for different intermolecular distances. Excellent agreement is observed between the ReaxFF potential and the \textit{ab initio} result for large intermolecular distances $d$. The ReaxFF fit gives qualitative agreement, although with decreasing accuracy, to the \textit{ab initio} results with decreasing $d$. In particular, the inner-wall potential for small interatomic distances ($r_b < \approx 1.2$ Å) agreement is excellent for all $d$ shown. This is significant because MD/QCT trajectories accessing these high energy areas of the ReaxFF potential energy surface will be more likely to result in dissociations.

Figure 6.2(b) shows the ReaxFF potential and corresponding \textit{ab initio} MS-CASPT2 calculations of the 4N system versus varying intermolecular distance $d$ for various bond lengths $r_b$, where $r_a = 1.098$ Å, $\theta_a = \theta_b = 90^\circ$, and $\phi = 0^\circ$. Excellent agreement is obtained between the ReaxFF potential and the \textit{ab initio} results. Note that Figs. 6.2(a) and 6.2(b) display only a very small subset of the total \textit{ab initio} datapoints that the ReaxFF potential was fit to, and therefore do not represent the overall fit of the 6-dimensional surface, but they give a representation of the accuracy of the fit.
(a) Potential energy versus bond length $r_b$ for various intermolecular distances $d$, where $r_a = r_b = 1.098 \, \text{Å}$, $\theta_a = \theta_b = 90^\circ$, and $\phi = 0^\circ$. 

(b) Potential energy versus intermolecular distance $d$ for various bond lengths $r_b$, where $r_a = 1.098 \, \text{Å}$, $\theta_a = \theta_b = 90^\circ$, and $\phi = 0^\circ$.

Fig. 6.2. Potential energy of the 4N system as determined from the ReaxFF potential (solid lines) and accurate ab initio calculations [13] (symbols).

Figure 6.3 compares the ReaxFF intermolecular potential to the crude Billing and Fisher [120] intermolecular potential used in the FHO-CR [66] internal energy relaxation model, where $r_a = r_b = 1.098 \, \text{Å}$, $\theta_a = \theta_b = 90^\circ$, and $\phi = 0^\circ$. While the ReaxFF potential agrees well with the accurate ab initio results, the Billing and Fisher intermolecular potential diverges and is significantly greater than the ab initio results for $d < \approx 3.0 \, \text{Å}$. For instance, the ReaxFF potential is $\approx D_e$ at $d = 1.6 \, \text{Å}$ for the ReaxFF potential, whereas the Billing and Fisher potential is $\approx D_e$ at $d = 2.4 \, \text{Å}$. This significant difference between the two intermolecular potentials will ultimately impose differences in resulting dissociation and internal energy relaxation models, as will be discussed in Section 6.7.
Fig. 6.3. Potential energy of the 4N system versus intermolecular distance $d$, where $r_a = r_b = 1.098 \text{ Å}$, $\theta_a = \theta_b = 90^\circ$, and $\phi = 0^\circ$ as determined from the ReaxFF potential, accurate ab initio calculations [13], and Billing and Fisher intermolecular potential employed by the FHO-CR model.

6.2.2 Determination of $v, J$ Levels

In DSMC, quantized energy levels have typically been determined as the sum of a harmonic oscillator vibrational component dependent on vibrational quantum number $v$ and a rigid rotor rotational component dependent on rotational quantum number $J$. Because the ReaxFF potential energy surface is more sophisticated than the simple harmonic oscillator and rigid rotor assumption, rovibrational levels based on the ReaxFF potential are needed. The rovibrational levels can be determined using the WKB (Wentzel, Kramers, Brillouin) method [121], as previously demonstrated for the $\text{N}_2-\text{N}_2$ potential of Jaffe et al. [14]. The following relation defines the rovibrational
energy levels $E(v, J)$ according to the WKB method,

$$\frac{1}{\hbar} \int_{r_-}^{r_+} [2\mu(E(v, J) - U(r))]^{1/2} dr = \pi \left( v + \frac{1}{2} \right), \quad (6.1)$$

where $r_-$ and $r_+$ are the inner and outer vibrational turning points (i.e. the minimum and maximum bond lengths for the rovibrational level), respectively, $\mu$ is the reduced mass of the N-N atom pair, and $U(r)$ can be written as the sum of two terms $U(r) = V(r) + E_{rot}$, where $V(r)$ is the $N_2$ potential computed with no rotation ($J = 0$) at radius $r$, and $E_{rot}$ is the rotational energy, defined in the rigid rotator convention

$$E_{rot} = \frac{\hbar^2 J(J + 1)}{2\mu r^2}. \quad (6.2)$$

Following the WKB solution methodology presented in Appendix C, it was found that the ReaxFF potential has 9373 total rovibrational levels, compared to 9399 total rovibrational levels predicted by the Jaffe potential, a difference of 0.2 %. The ReaxFF potential has 6930 bound rovibrational levels for which the internal energy is less than the dissociation energy, and 2443 quasi-bound rovibrational levels that have internal energy greater than the dissociation energy, usually characterized by highly rotationally excited levels compared to the vibrational energy. In comparison, the Jaffe potential predicted 7437 bound rovibrational levels and 1962 quasi-bound levels. It is assumed that the ReaxFF potential has a higher proportion of quasi-bound levels due to its relatively long asymptotic potential in the dissociation region, which allows for more high rotational energy levels.
A comparison of the rovibrational levels between the work of Jaffe [122] and this work is shown in Fig. 6.4. The dashed lines represent the contour levels of rovibrational energy level for the Jaffe potential, and the solid lines represent the contour lines of the ReaxFF potential. The solid line boundaries represent the maximum rotational level $J$ possible for each vibrational level $v$, with the red boundary for the Jaffe potential and the purple boundary for the ReaxFF potential. In general, there is good qualitative agreement in the prediction of the energy levels between the two potentials. However, for the low vibrational levels ($v < 10$), the ReaxFF potential predicts more rotational levels than the Jaffe potential, and the maximum vibrational level for the ReaxFF potential is 52, compared to 60 for the Jaffe potential.

Figure 6.5(a) shows the energy levels versus $J$ for several fixed $v$ levels as determined from both the ReaxFF and Jaffe potentials. Good agreement is observed between the two methods, and the maximum $J$ level decreases with increasing $v$, as expected. Figure 6.5(b) shows the energy levels versus $v$ for several fixed $J$ levels as determined from both the ReaxFF and Jaffe potentials and, again, good agreement is observed between the two potentials.

Table 6.1 shows the number of bound and quasi-bound $J$ levels for various $v$ determined from the ReaxFF potential. The number of possible $J$ levels decreases with increasing $v$ level, as expected and shown in Fig. 6.5(a). It is also found that the proportion of levels that are bound decreases with increasing $v$ level greater than 10. This is because quasi-bound levels are typically characterized by molecules with much higher rotational than vibrational energy. Table 6.2 shows that rotational level spacing increases and vibrational spacing decreases with increasing $J$, as expected.
Table 6.1. Total number of rotational $J$ levels for various $v$ levels, the number of bound and quasi-bound levels, and percentage of levels that are bound as determined from the WKB method with the ReaxFF potential energy surface.

<table>
<thead>
<tr>
<th>$v$</th>
<th>Total $J$ levels</th>
<th>Bound</th>
<th>Quasi-bound</th>
<th>% bound</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>331</td>
<td>212</td>
<td>119</td>
<td>64.0</td>
</tr>
<tr>
<td>10</td>
<td>231</td>
<td>187</td>
<td>44</td>
<td>81.0</td>
</tr>
<tr>
<td>20</td>
<td>205</td>
<td>155</td>
<td>50</td>
<td>75.6</td>
</tr>
<tr>
<td>30</td>
<td>169</td>
<td>125</td>
<td>44</td>
<td>74.0</td>
</tr>
<tr>
<td>40</td>
<td>123</td>
<td>88</td>
<td>35</td>
<td>71.5</td>
</tr>
<tr>
<td>50</td>
<td>51</td>
<td>22</td>
<td>29</td>
<td>43.1</td>
</tr>
<tr>
<td>52</td>
<td>17</td>
<td>1</td>
<td>16</td>
<td>5.9</td>
</tr>
</tbody>
</table>

Table 6.2. Further details on $N_2$ ($v, J$) levels determined from the ReaxFF potential, including the maximum $v$ for each $J$, vibrational spacing, and rotational spacing

<table>
<thead>
<tr>
<th>$J$</th>
<th>$v_{max}$</th>
<th>$E(0, J)$</th>
<th>$E(v_{max}, J)$</th>
<th>$E(1, J) - E(0, J)$</th>
<th>$E(0, J + 1) - E(0, J)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>52</td>
<td>3.801</td>
<td>231.02</td>
<td>7.6</td>
<td>0.01</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>17.69</td>
<td>234.39</td>
<td>7.6</td>
<td>0.55</td>
</tr>
<tr>
<td>90</td>
<td>45</td>
<td>47.89</td>
<td>240.44</td>
<td>7.6</td>
<td>0.96</td>
</tr>
<tr>
<td>150</td>
<td>34</td>
<td>122.39</td>
<td>257.82</td>
<td>7.3</td>
<td>1.51</td>
</tr>
<tr>
<td>210</td>
<td>18</td>
<td>226.40</td>
<td>286.36</td>
<td>5.0</td>
<td>1.93</td>
</tr>
<tr>
<td>330</td>
<td>0</td>
<td>443.96</td>
<td>443.96</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
6.2.3 Bin Model for Grouping Rovibrational States

An MD/QCT study generating transition probabilities for all possible rovibrational combinations would be a prohibitively expensive undertaking due to the extremely high number of possible transitions ($\approx 10^{15}$). Moreover, the use of such a database in DSMC simulations would be impractical due to the added exorbitant computational cost and memory requirements. By strategically binning energy levels together, however, the number of necessary trajectory computations can be reduced to a manageable number while still accurately resolving complex internal energy relaxation mechanics. In an energy bin model, dissociation probabilities are determined for collisions with unique
relative velocity and energy bin combinations, rather than unique relative velocity and rovibrational level combinations. Each of the energy levels within a bin are assumed to have equivalent characteristics. For example, the probabilities of a jump to a different energy bin or probability of dissociation of all energy levels within a bin are assumed to be equal for a given collision defined by a relative velocity and initial collision pair internal energy bin indices.

The bin model choice should not significantly affect the internal energy relaxation and dissociation processes of interest for $N_2-N_2$ collisions. Therefore, the bin model should well resolve Maxwell-Boltzmann internal energy distributions for the temperatures expected in hypersonic flight and should lead to solutions that are independent of the number of bins used. Magin et al. [72] and Munafó et al. [73] concluded that using
40 energy bins for the N\textsubscript{2} molecule in N\textsubscript{2}-N internal energy relaxation and dissociation simulations was sufficient to result in converged, accurate solutions. As such, 40 bound energy bins were initially considered in the Jaffe et al. N\textsubscript{2}-N\textsubscript{2} studies [14], and 40 bound energy bins are therefore also used in this work, each with a constant width of 5.75 kcal/mol. As shown above, quasi-bound states are also possible, which are expected to be significant contributors to high-temperature dissociation, so six quasi-bound energy bins with increasing width will also be considered, giving 46 total internal energy bins for this study. Table 6.3 gives the details on the width and range of internal energies in each bin. The quasi-bound bin widths were chosen such that each bin contained approximately the same number of levels. Because the six quasi-bound bins must contain the rovibrational energy levels ranging from 230 kcal/mol to the maximum determined ReaxFF rovibrational level of \( E(v = 0, J = 330) = 443.96 \) kcal/mol, the quasi-bound energy bins are wider than the constant-width bound energy bins. Wider bin widths are feasible because, first, the quasi-bound states will be less likely than those that are bound and, second, they are only possible at high-temperatures \( T > \approx 15,000 \) K associated with relatively flat Boltzmann distributions for internal energy, as will be shown later. Therefore, there are less restrictions on energy bin resolution for these high-lying levels.

The ReaxFF generated potential has 9373 \((v, J)\) rovibrational levels, as explained in Section 6.2.2. Using a global energy level index \( i \), the rovibrational energy levels \( v_i \) and \( J_i \) and corresponding energies \( E_i \) are sorted into ascending \( E_i \) order, where \( E_i = E(v_i, J_i) \), similar to the methodology used in the previous nitrogen bin models of Magin [72] and Munafó [73]. If \( I_b \) is the set of \( i \) indices within energy bin \( b \), the degeneracy
Table 6.3. \( N_2 \) internal energy bin width and ranges.

<table>
<thead>
<tr>
<th>Bin Index ( b )</th>
<th>Bin Width [kcal/mol]</th>
<th>Energy range [kcal/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bound bins</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-40</td>
<td>5.75</td>
<td>5.75 ((b-1)) to 5.75 (b)</td>
</tr>
<tr>
<td>41</td>
<td>5.75</td>
<td>230 to 235.75</td>
</tr>
<tr>
<td>42</td>
<td>7.75</td>
<td>235.75 to 243.5</td>
</tr>
<tr>
<td>43</td>
<td>10.5</td>
<td>243.5 to 254</td>
</tr>
<tr>
<td>44</td>
<td>14.0</td>
<td>254 to 268</td>
</tr>
<tr>
<td>45</td>
<td>23.0</td>
<td>268 to 291</td>
</tr>
<tr>
<td>46</td>
<td>153.0</td>
<td>291 to 444</td>
</tr>
<tr>
<td>Quasi-bound bins</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

of each bin, \( g_b \), can be defined by the sum of the degeneracies of its constituent energy levels

\[
g_b = \sum_{i \in I_b} g_i, \tag{6.3}
\]

where \( g_i = (2J_i + 1)g_i^{NS} \) and the nuclear spin degeneracy \( g_i^{NS} \) is 6 for even \( J_i \) and 3 for odd \( J_i \). The average internal energy of each bin, \( \bar{E}_b \), is then

\[
\bar{E}_b = \frac{\sum_{i \in I_b} g_i E_i}{g_b}. \tag{6.4}
\]

The average vibrational level of each bin, \( \bar{v}_b \), is computed by substituting \( \bar{v}_b \) for \( \bar{E}_b \) and \( v_i \) for \( E_i \) in Eq. 6.4. The number of levels within each bin, bin degeneracy, average internal energy, and average vibrational level are shown in Fig. 6.6. The number of levels within each bound bin (bins 1-40), degeneracy, and average vibrational level rise monotonically with bin index. The relationship between \( \bar{v}_b \) and bin index is significant because it implicitly enables vibrational level resolution of dissociation and relaxation.
processes. For the quasi-bound bins (41-46), the average vibrational level decreases with increasing bin index, however. This is because internal energy increases for quasi-bound levels are more likely to correspond with increases in rotational energy because increases in vibrational energy will tend to lead to dissociated molecules. The average energy in each bound bin rises monotonically and approximately linearly with bin index, as expected due to the constant width of 5.75 kcal/mol for the bound energy bins.

![Graph](image)

**Fig. 6.6.** Characteristics of the bin model for $N_2$ internal energy levels based on the ReaxFF potential. Bin degeneracy, average internal energy, and the number of levels in each bin are plotted against the left axis, and the average vibrational level is plotted against the right axis. There are 46 energy bins. The first 40 bins are bound energy bins with constant width of 5.75 kcal/mol. The final six bins are quasi-bound bins with increasing width.
The thermal weight associated with each bin, or relative population of each bin assuming a Maxwell-Boltzmann distribution for internal energy at the rovibrational temperature $T_{\text{int}}$ is,

$$\frac{\bar{n}_b}{n_{N_2}} = \frac{g_b \exp \left[ -\frac{\bar{E}_b}{k_BT_{\text{int}}} \right]}{\bar{Q}},$$

(6.5)

where $\bar{n}_b$ is the number density of particles in bin $b$, $n_{N_2}$ is the total molecular number density and the total partition function, $\bar{Q}$, is

$$\bar{Q} = \sum_{b=1}^{46} g_b \exp \left[ -\frac{\bar{E}_b}{k_BT_{\text{int}}} \right].$$

(6.6)

The thermal weight of each bin at various temperatures that may be expected in hypersonic shocks is shown in Fig. 6.7. The bin model provides good resolution of the internal energy distribution for each of the displayed temperatures. As temperature increases, bin population shifts from the lower energy bins to the higher energy bins. Temperatures above 11,000 K tend to lead to $N_2$ dissociation and relatively significant proportions of quasi-bound $N_2$ molecules. Because the quasi-bound energy bins are wider than the bound energy bins, there is a slight hump in the distribution for the quasi-bound bins for temperatures above 11,000 K.

### 6.3 Application of the Bin Model in MD/QCT

The governing equations for the MD/QCT method are Hamilton’s equations (Eqs. 1.11 and 1.12), which are solved using the fourth-order Runge-Kutta method detailed in Appendix A. Each case in this MD/QCT study consists of a large set of
Fig. 6.7. Thermal weight of each bin at various internal temperatures.

trajectories defined by common relative collision velocities $c_r$ and initial molecular internal energy bins $b_A$ and $b_B$, where the subscripts $A$ and $B$ represent each of the initial $N_2$ molecules. The individual trajectories for each case have unique combinations of impact parameters, rovibrational levels, and molecular orientations that are determined by the initial coordinates and momenta of the constituent atoms. The impact parameters and molecular orientations are determined through Monte Carlo sampling detailed in Appendix B. The rovibrational levels for each molecule are chosen from a uniform, equal distribution of the levels within each internal energy bin. Once the rovibrational $(v, J)$ levels are selected for a given trajectory, initial bond lengths and atomic momenta are determined using the methodology detailed in Appendix B.5.
Upon completion of each MD/QCT trajectory, the interatomic distances of the system particles determine which, if any, reactions have occurred. If an atom is more than 3.5 Å from the nearest atom, it is considered dissociated. For the N₂-N₂ system, two distinct dissociation reactions are possible:

\[ N₂ + N₂ \rightarrow N₂ + 2N, \]  
\[ N₂ + N₂ \rightarrow 4N, \]  

where Eq. 6.7 will be referred to as the single dissociation process and Eq. 6.8 as the double dissociation process. Following Eq. 1.13, the number of trajectories resulting in reaction \( s \), \( N_s(b_A, b_B, c_r) \), is counted for each case and the corresponding reaction cross section \( \sigma_{s,MD}(b_A, b_B, c_r) \) for reaction path \( s \) is determined by

\[ \sigma_{s,MD}(b_A, b_B, c_r) = \pi B_{\text{max}}^2 \frac{N_s(b_A, b_B, c_r)}{N_T(b_A, b_B, c_r)}, \]  

where \( B_{\text{max}} \) is the maximum impact parameter and \( N_T \) is the total number of trajectories that are sampled in that case. For the single dissociation reaction, the reaction cross section is independent of the final internal energy of the remaining N₂ molecule.

Similarly, by determining the post-collision internal energy of the colliding nitrogen molecules for each trajectory in a given case, energy bin-to-bin cross sections can be determined. The bin-to-bin cross sections \( \sigma(b_A, b_B, c_r \rightarrow b'_A, b'_B) \) give the cross section for a collision with initial internal energy bins of \( b_A \) and \( b_B \) and a relative velocity \( c_r \).
resulting in post-collision internal energy bins of $b'_A$ and $b'_B$, and is defined by

$$
\sigma(b_A, b_B, c_r \rightarrow b'_A, b'_B) = \pi B^2 \max \frac{N(b_A, b_B, c_r \rightarrow b'_A, b'_B)}{N_T(b_A, b_B, c_r)},
$$

(6.10)

where $N(b_A, b_B, c_r \rightarrow b'_A, b'_B)$ is the number of trajectories that result in post-collision internal energy bin values of $(b'_A, b'_B)$. Therefore, if $b'_A > b_A$, the internal energy bin value of molecule $A$ increases after a collision and if $b'_A < b_A$, the internal energy bin value of molecule $A$ decreases. In the event of an exchange reaction, in which the colliding $N_2$ molecules swap N atoms, the $A$ and $B$ labels are given to the newly created $N_2$ molecules, and post-collision internal energy bins, $b'_A$ and $b'_B$, are determined. Exchange reactions resulting in $(b'_A, b'_B)$ are included in the $N(b_A, b_B, c_r \rightarrow b'_A, b'_B)$ count.

The non-reacting collision cross section, $\sigma_{coll,MD}(b_A, b_B, c_r)$ is computed using the method of Tokumasu and Matsumoto [69, 70] described by Eq. 1.14. The total cross section for each case is then the sum of the collision cross section and each of the reaction cross sections,

$$
\sigma_{tot,MD}(b_A, b_B, c_r) = \sigma_{coll,MD}(b_A, b_B, c_r) + \sum_{s=1}^{N_R} \sigma_{s,MD}(b_A, b_B, c_r).
$$

(6.11)

The probability of a given reaction $s$ occurring for each collision condition is needed for DSMC simulations and is given as the ratio of the process cross section over the total cross section,

$$
P_{s,MD}(b_A, b_B, c_r) = \frac{\sigma_{s,MD}(b_A, b_B, c_r)}{\sigma_{tot,MD}(b_A, b_B, c_r)}.
$$

(6.12)
Similarly, the probability of a collision with initial internal energy bins of $b_A$ and $b_B$ and a relative velocity $c_r$ resulting in post-collision internal energy bins of $b'_A$ and $b'_B$ is

$$P(b_A, b_B, c_r \rightarrow b'_A, b'_B) = \frac{\sigma(b_A, b_B; c_r \rightarrow b'_A, b'_B)}{\sigma_{tot, MD}(b_A, b_B, c_r)}.$$  \hspace{1cm} (6.13)

For comparison to experimental shock-tube data, corresponding equilibrium reaction rates based on the MD/QCT results will need to be computed. Using the coarse grain bin model described in Section 6.2.3, the rate for a given process $s$ at translational temperature $T$ and internal, or rovibrational, temperature $T_{int}$ is determined using,

$$k_s(T_{int}, T) = \sum_{b_A=1}^{46} \left[ \frac{\bar{n}_b A}{n_{N_2}} \sum_{b_B=1}^{46} \left( \frac{\bar{n}_b B}{n_{N_2}} \int_0^\infty f(c_r) \sigma_s(b_A, b_B, c_r) c_r dc_r \right) \right], \hspace{1cm} (6.14)$$

where the thermal weights of the bins are defined by Eq. 6.5 and the Maxwell-Boltzmann distribution function for relative velocity, $f(c_r)$ is given by Eq. 5.5.

For these trajectory studies, all 1081 possible unique initial internal energy bin combinations were computed for 11 relative velocities ranging from 1-20 km/s, giving 11891 total MD/QCT $N_2$-$N_2$ cases. The optimal numerical simulation parameters were determined through a rigorous sensitivity analysis similar to the one employed in Section 5.3 for the N-$N_2$ pair. Each case consisted of 10,000 trajectories that each started with an initial target-collider distance of 10 Å. The maximum impact parameter used was 4 Å, meaning that computed cross sections have a resolution of 0.005 Å$^2$. Timestep sizes were dependent on relative velocity in order to accurately model time-dependent collider-target interactions while minimizing computational cost: 0.25 fs for $c_r \geq 14$. 
km/s, 0.4 fs for 10 km/s ≤ \( c_r < 14 \) km/s, and 0.5 fs for \( c_r < 10 \) km/s. For each case, enough timesteps were simulated such that the expected final post-collision distance between target and collider is 10 Å. The details of the sensitivity analysis are given in Appendix D.2.

### 6.4 MD/QCT-Computed Reaction and Internal Energy Excitation Rates

Equilibrium reaction rates are determined from the MD/QCT results using Eq. 6.14, setting \( T_{int} = T \), and compared to the shock tube data of Hanson [10] (valid for 5,700 K < \( T < 12,000 \) K) and Appleton [9] (8,000 K < \( T < 15,000 \) K), Byron [11] (6,000 K < \( T < 9,000 \) K), and Cary (6,000 K < \( T < 10,000 \) K) in Fig. 6.8. The equilibrium reaction rates determined from the Jaffe MD/QCT studies [14] and QK model [8] with \( \theta_v = 3371 \) K for \( \text{N}_2 \) are also displayed. The MD/QCT equilibrium rate, represented by the solid black curve, agrees well with the experimental data in their respective temperature ranges, providing a measure of validation for the MD/QCT method. The difficulty in experimentally obtaining accurate and precise reaction rates is demonstrated by the variance of up to one order of magnitude in the experimentally determined rates. The MD/QCT reaction rates of this study are 1.4-3.6 times greater than the Jaffe computed rates. In relation to the precision of the experimentally determined rates, the MD/QCT results of this study agree reasonably well with the Jaffe results. It is also observed that the QK model predicts reaction rates greater than nearly all the experimentally determined reaction rates. Therefore, it is determined that the MD/QCT results of this work are able to reliably replicate experimentally determined
equilibrium reaction, do so much better than the QK model, and also agree reasonably well to the work of Jaffe [14].

MD/QCT reaction rates computed for thermal nonequilibrium where $T_{int} \neq T$, with fixed internal temperatures $T_{int}$ of 1000 K and 5000 K and for thermal equilibrium where $T_{int} = T$ are shown in Fig. 6.9. They are compared to the phenomenological Park two-temperature model [3] commonly employed to determine nonequilibrium reaction rates in CFD that was presented in Section 5.5 and is governed by Eq. 5.6. In the computation of the MD/QCT nonequilibrium rates, it is assumed that $T_{int} = T_v = T_r$. Recall that, in the MD/QCT energy bin approach used in this study, rovibrational levels are coupled together within bins, so a combined internal, or rovibrational, temperature is used, as defined in Eq. 6.5. It can be seen that the MD/QCT nonequilibrium reaction rates decrease as internal temperatures decrease. The MD/QCT equilibrium reaction rates agree well with the Park model, as expected, because the Park model uses Arrhenius parameters given in Table 5.3 that are fits to the experimentally determined rates that were already shown to be in reasonable agreement with the MD/QCT rates in Fig. 6.8. However, when thermal nonequilibrium is introduced, the MD/QCT reaction rates significantly depart from the rates of the Park model. This effect is most prominently observed for strong thermal nonequilibrium, i.e. where there is a significant difference in the translational and internal temperatures. When the internal temperature is set to 1000 K, the Park model predicts nonequilibrium rates several orders of magnitude less than the MD/QCT rates. As internal temperatures increase to 5000 K, the differences between the MD/QCT and Park nonequilibrium rates decrease to less than an order of magnitude for the displayed temperature range, but the MD/QCT rates are
still higher than those predicted by the Park model. The significant discrepancy between the MD/QCT results and Park model was also shown for the N + N$_2$ → 3N reaction in Section 5.5 and Magin et al. [107]. Therefore, while the phenomenological Park model does address the dependence of reaction rates on both vibrational and translational temperatures, it significantly under-predicts reaction rates for strong thermal nonequilibrium conditions compared to the MD/QCT results.

![Graph showing reaction rate coefficients](image)

Fig. 6.8. N$_2$ + N$_2$ → N$_2$ + 2N reaction rate coefficients in thermal equilibrium computed from the MD/QCT method compared to the shock-tube data of Appleton [9], Hanson [10], Byron [11], and Cary [12]. Experimental reaction rate coefficients are shown only for the relevant temperature range used in each study, respectively. The reaction rate coefficients for the Jaffe MD/QCT studies and the QK model [8] are also shown.
Fig. 6.9. $N_2 + N_2 \rightarrow N_2 + 2N$ reaction rate coefficients as a function of temperature for thermal equilibrium ($T_{\text{int}} = T_{v} = T$) and thermal nonequilibrium with $T_{\text{int}} = 1000$ K and $T_{\text{int}} = 5000$ K, determined by the MD/QCT results of this study and the Park two-temperature model [3], where $T_{v}$ is the vibrational temperature.

The bin-specific dissociation rate coefficients versus temperature are shown in Fig. 6.10, clearly showing the strong dependence on initial internal energy bin value on the dissociation process. The dissociation rate increases with increasing internal energy bin, as expected, and the highest reaction rates shown are for the quasi-bound bin ($b = 41$). Because average vibrational level increases with increasing internal energy bin index, as shown in Fig. 6.6, this indicates that bin-resolved dissociation probabilities and rates also implicitly resolve probabilities and rates dependent on vibrational levels. Recall that the probability of $N_2$ dissociation is known to increase with increasing vibrational energy [3]. Also, recall that bin population shifts from lower energy bins to higher energy bins with increasing temperature, as seen in Fig. 6.7. As such, the bin averaged rate,
which is identical to the “MD/QCT” curve in Fig. 6.8, tends to agree better with rates for relatively low internal energy bins at lower temperatures and, conversely, agrees better with rates for relatively high internal energy bins at higher temperatures.

![Graph showing bin-specific reaction rate coefficients versus temperature](image)

**Fig. 6.10.** Bin-specific reaction rate coefficients versus temperature for the $N_2 + N_2 \rightarrow N_2 + 2N$ process, where $b_A = b_B = b$.

The explicit effect of inclusion of the quasi-bound rovibrational levels is seen in Fig. 6.11, where it can be seen that the dissociation rate coefficient is greater when considering the quasi-bound rovibrational levels. This is expected because quasi-bound levels are characterized by their very high internal energies and, therefore, relatively low translational energies are needed for dissociation. Recall that the quasi-bound bin gave the highest bin-specific dissociation rate shown in Fig. 6.10. At low temperatures,
however, these quasi-bound states are not likely to exist, as shown in Fig. 6.7. Therefore, at low temperatures ($T \approx 10,000$ K), there is relatively little difference between the rate coefficients with and without the quasi-bound levels. The quasi-bound levels are more likely to be populated as temperature increases, so, as temperature increases, the effect of the quasi-bound levels increases such that the quasi-bound levels contribute over 40% of dissociations for $T > 40,000$ K. Note that the “MD/QCT” curve in Fig. 6.8 considers both bound and quasi-bound levels and is identical to the corresponding single dissociation rates considering both bound and quasi-bound levels of Fig. 6.11.

Figure 6.11 also shows the comparison of the $N_2 + N_2 \rightarrow N_2 + 2N$ and $N_2 + N_2 \rightarrow 4N$ reaction rate coefficients in thermal equilibrium computed from the MD/QCT method. It is observed that the double dissociation process is mostly negligible for low temperatures, as its rate coefficient is several orders of magnitude less than the dominant single dissociation process. However, for $10,000/T$ less than approximately 0.5, the double dissociation rate coefficient comes within approximately two orders of magnitude of the single dissociation rate. Therefore, for the hyperthermal conditions expected for some Earth re-entry flows, the double dissociation process may be an important consideration for accurately modeling the flowfield physics where temperatures are greater than approximately 20,000 K. Lastly, for all temperatures, the exchange reaction rate coefficient is less than the single dissociation rate coefficient, yet within an order of magnitude, and greater than the double dissociation rate coefficient.

Turning to the MD/QCT internal energy relaxation rates obtained using the bin model, the thermal equilibrium rate coefficients for either one (and only one) of the colliding $N_2$ molecules changing its energy bin, $b$, are displayed in Fig. 6.12. First, the
Fig. 6.11. Various reaction rate coefficients. The effect of computing the single dissociation process using only the bound energy levels versus using both bound and quasi-bound energy levels is examined. Additionally, the exchange and double dissociation reaction rate coefficients are shown.

rate of internal energy transfer increases for all examined $|b' - b| = m$, but the relaxation rates decrease as $m$ increases, where $|b' - b| = m$. Significantly, the relaxation rates for $b' - b = +m$ are approximately equal to the rates for $b' - b = -m$. This indicates that the probabilities of $N_2$ molecules increasing bin index by $m$ or decreasing bin index by $m$ after collisions are approximately equal, as expected in thermal equilibrium. The total weighted excitation and de-excitation rate coefficients, $k_{ex}$ and $k_{de}$, respectively, can be approximated by

$$k_{ex} = \sum_{m=1}^{45} mk_{\Delta b=m},$$

(6.15)

$$k_{de} = \sum_{m=-45}^{-1} mk_{\Delta b=m}.$$  

(6.16)
The ratio of the approximated total excitation and de-excitation rate coefficients is shown in Fig. 6.13. The $k_{ex}/k_{de}$ ratio is approximately equal to unity for all temperatures studied, as also expected in thermal equilibrium.

![Graph.png](attachment:Graph.png)

Fig. 6.12. Thermal equilibrium rate coefficients for $N_2$-$N_2$ internal energy transfer, examining different values of $m$, where $\Delta b = b' - b = m$ for either one of the $N_2$ molecules.

### 6.5 Generation of DSMC $N_2$-$N_2$ Collision, Reaction, and Internal Energy Exchange Models Based on MD/QCT

In this section, new models for DSMC $N_2$-$N_2$ reaction probabilities, collision cross sections, and internal energy exchange are introduced based on the MD/QCT
Fig. 6.13. Ratios of thermally averaged rate coefficients of N$_2$ internal energy bin jumps for either of the colliding N$_2$-N$_2$ molecules. The excitation and de-excitation rate coefficients $k_{ex}$ and $k_{de}$ are defined in Eqs. 6.15 and 6.16, respectively.

studies with rovibrational states grouped into internal energy bins. First, total collision cross sections, which determine collision frequency in DSMC, will be computed and will be shown to be well-fit to the VHS form. Then, the MD/QCT-computed reaction probabilities will be presented. A database of these probabilities can be used in DSMC to replace the existing commonly used phenomenological chemistry models, such as the TCE [4] or QK [8] models. Finally, internal energy relaxation cross sections will be generated that can be used to replace the LB [57] or FHO/FHO-CR [15, 66] models.
6.5.1 Collision Cross Sections

Figure 6.14 shows the collision, reaction, and total cross sections versus relative velocity for the N$_2$-N$_2$ pair with initial internal energy bins $b_A = 8$ and $b_B = 24$, which contain rovibrational levels ranging from 40.25-46 kcal/mol and 132.25-138 kcal/mol, respectively, where each bin is expected to contain at least 0.5% of the N$_2$ population for equilibrium temperatures above 11,000 K, as shown in Fig. 6.7. The collision cross section decreases with increasing velocity, as expected. In order for a dissociation reaction to occur, the total collision energy must be greater than the N$_2$ dissociation energy, where the total collision energy, $E_c$, is defined as

$$E_c = \frac{1}{2}\mu c_r^2 + E_{i,A} + E_{i,B}. \quad (6.17)$$

The velocity needed to raise the total collision energy above the N$_2$ dissociation energy is 5.5 km/s. As such, the single dissociation (N$_2$+N$_2$→N$_2$+2N) cross section increases with increasing velocity for $c_r > 5.5$ km/s, and is zero for $c_r < 5.5$ km/s. The velocity needed to raise the total collision energy to twice the dissociation energy is 12.9 km/s, so the double dissociation (N$_2$+N$_2$→4N) cross section is non-zero only for the two studied relative velocities for which $c_r > 12.9$ km/s and increases with increasing velocity. However, the single dissociation cross section is the dominant reaction cross section for all relative velocities studied in these cases. At velocities low enough such that dissociation reactions are not possible, the total cross section is equal to the collision cross section.

Figure 6.15 shows the total cross section versus relative velocity for the N$_2$-N$_2$ collision pair. Each symbol type represents MD/QCT results for unique initial internal
Fig. 6.14. The collision, reaction, and total cross sections versus relative velocity for the $N_2$-$N_2$ pair with $b_A = 8$ ($E_i \in [40.25, 46 \text{ kcal/mol}]$), $b_B = 24$ ($E_i \in [132.25, 138 \text{ kcal/mol}]$). The red curve represents the single dissociation cross section for the $N_2 + N_2 \rightarrow N_2 + 2N$ path and the blue curve represents the double dissociation cross section for the $N_2 + N_2 \rightarrow 4N$ path.

energy bin pairs. It is observed that the computed total collision cross sections do not depend strongly on the initial internal energies in the collision, but exhibit a power-law relationship with respect to relative velocity, which allows the results to be fit to the VHS form of Eq. 1.1. The MD/QCT VHS fit is represented by the black curve, which had a coefficient of determination $R^2$ value of 0.993, indicating that the MD/QCT VHS fit agrees with the corresponding results very well. The MD/QCT VHS fit also agrees well with the Bird [4] VHS parameters based on low-temperature viscosity data and VHS parameters based on numerically determined high-temperature viscosity computations (up to 10,000 K) of Stallcop [7]. Specifically, there is a 14.3% average relative difference
between the MD/QCT VHS fit and the Bird VHS curve at each of the 11 studied relative velocities, compared to only 7.2% average relative difference between the MD/QCT VHS fit and the Stallcop VHS curve. The MD/QCT VHS fit’s better agreement to the Stallcop VHS curve is expected because each are based on higher-temperature assumptions than the Bird VHS curve. The MD/QCT fit, Bird, and Stallcop VHS parameters are given in Tbl. 6.4, and the MD/QCT fit is used in the calculation of the reaction probabilities discussed in the next subsection.

![Graph](image)

Fig. 6.15. MD/QCT-computed total cross sections for the N₂-N₂ pair for various initial internal energy pairs. The MD/QCT results fit to the VHS form of Eq. 1.1 are compared to established VHS curves for the N₂-N₂ pair using Bird [4] and Stallcop [7] VHS parameters.
Table 6.4. VHS parameters for N$_2$-N$_2$ collisions.

<table>
<thead>
<tr>
<th>Model</th>
<th>$\omega$</th>
<th>$d_{ref}$ [Å]</th>
<th>$T_{ref}$ [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MD/QCT VHS Fit</td>
<td>0.725</td>
<td>3.768</td>
<td>1000</td>
</tr>
<tr>
<td>Bird [4]</td>
<td>0.74</td>
<td>4.11</td>
<td>273</td>
</tr>
<tr>
<td>Stallcop [7]</td>
<td>0.68</td>
<td>3.58</td>
<td>1000</td>
</tr>
</tbody>
</table>

6.5.2 Reaction Probabilities and Post-Dissociation Internal Energy Distributions

Figure 6.16(a) shows the MD/QCT-computed probability (defined in Eq. 6.12) of the N$_2$ + N$_2$ → N$_2$ + 2N reaction versus $\bar{E}_c$, where $\bar{E}_c = \bar{E}_A + \bar{E}_B + E_{tr}$ and $\bar{E}_A$ and $\bar{E}_B$ are the average initial internal energies of molecules A and B defined by Eq. 6.4, respectively. Dissociation is only possible when the total collision energy, $E_c$, is greater than the N$_2$ dissociation energy of 230 kcal/mol. In general, the probability of dissociation tends to increase with increasing total collision energy. However, for a given collision energy, the probability of dissociation can vary significantly, due to possible differences in the partitioning of the energy in the collision. Collisions involving molecules with initial internal energies near or above the dissociation energy are more likely to dissociate than those with less excited molecules. This is observed more clearly in Fig. 6.16(b), where the MD/QCT-computed probability of the dissociation reaction is shown versus relative velocity for various initial internal energy pairs, where $b_A = b_B = b$. In general, the probability of dissociation increases with increasing initial internal energy and with increasing relative velocity. The highest dissociation probabilities shown are for the cases with quasi-bound initial internal energy levels ($b_A = b_B = 41$). The dissociation
probability approaches unity, but does not asymptote to unity with increasing relative velocity, which is particularly noticeable for the case where $b = 41$. It will be shown later that this is due to the increased influence of the double dissociation reaction path at very high collision energies, where both $N_2$ molecules dissociate, rather than only a single one.

![Graph](image)

(a) Reaction probability versus $\bar{E}_c$ for several relative velocities $c_r$

(b) Reaction probability versus relative velocity for several initial internal energy pairs, where $b_A = b_B = b$

**Fig. 6.16.** MD/QCT-computed reactions probabilities for the $N_2 + N_2 \rightarrow N_2 + 2N$ process.

Figure 6.17(a) and 6.17(b) show the MD/QCT reaction probabilities versus relative collision velocity and combined average initial internal energies $\bar{E}_A + \bar{E}_B$, respectively, compared to those determined using the TCE model [4] with Park [3] Arrhenius parameters and the QK model [8]. The MD/QCT-computed probability of dissociation
increases with increasing relative velocity and approaches unity, as shown in Fig. 6.17(a). However, the TCE model reaches a peak probability of dissociation of $\approx 0.7$ at $c_r \approx 12$ km/s, while the QK model predicts higher reaction probabilities than both the MD/QCT and TCE methods for all shown collision conditions in Fig. 6.17(a). Figure 6.17(b) again shows that the MD/QCT results predict increasing dissociation probability with increasing total initial internal energy. For low relative velocities, dissociations are only possible for collisions with a high degree of initial internal energies. It is noted in Fig. 6.17(b) that for each $(\bar{E}_A + \bar{E}_B)$ and $c_r$ pair, there may exist multiple dissociation probabilities.

Consider two separate collisions, each with a common $(\bar{E}_A + \bar{E}_B)$ and $c_r$. A collision involving a $N_2$ molecule that has a relatively high $E_i$ is more likely to dissociate than one in which both $N_2$ molecules have similar, lower $E_i$ values. Therefore, it is important to consider both internal energies separately, rather than just their combined values, when tabulating dissociation probabilities for use in future DSMC calculations. Again, the QK model predicts higher reaction probabilities than both the MD/QCT and TCE methods for all shown collision conditions in Fig. 6.17(b).

The internal energy distribution of the remaining $N_2$ molecule can also be determined in the trajectory studies. Use of the recorded post-dissociation internal energy distributions in DSMC may lead to more accurate modeling of the mechanics of the dissociation process than the LB/TCE method typically employed. The post-dissociation internal energy bin index is recorded for the remaining $N_2$ molecule for each single dissociation reaction and, for each case, a corresponding distribution of post-reaction bin indices is determined.
Relative Velocity [m/s]  

Dissociation Probability

10^{-6} 10^{-5} 10^{-4} 10^{-3} 10^{-2} 10^{0}

MD/QCT: $b_A = b_B = 7$
MD/QCT: $b_A = b_B = 19$
TCE: $b_A = b_B = 7$
TCE: $b_A = b_B = 19$
QK: $b_A = b_B = 7$
QK: $b_A = b_B = 19$

(a) Reaction probability versus relative velocity. Note that bins $b = 7$ and $b = 19$ contain rovibrational levels ranging from 34.5-40.25 kcal/mol and 103.5-109.25 kcal/mol, respectively.

(b) Reaction probability versus combined average initial internal energy $E_A + E_B$.

Fig. 6.17. MD/QCT $N_2 + N_2 \rightarrow N_2 + 2N$ reaction probabilities compared to the TCE model with Park Arrhenius parameters and the QK model.

Figure 6.18(a) shows the cumulative distribution of post-dissociation internal energy bin index of the remaining $N_2$ in a $N_2 + N_2 \rightarrow N_2 + 2N$ reaction for various relative velocities, where the initial pre-collision bin indices are $b_A = b_B = 21$. These bin indices are expected to contain at least 1% of $N_2$ molecules for $T \geq 11,000$ K, as shown in Fig. 6.7, and have relatively high probabilities of dissociation across a wide range of relative velocities, as shown in Fig. 6.16(b). As relative velocity increases, the distribution of post-reaction bin index shifts to the right, indicating that the remaining molecule is more likely to have higher internal energies for dissociations caused by higher relative velocities. The relative velocity, and thus total collision energy (defined in Eq. 6.17), also places a limit on the possible post-reaction bin index, as the post-collision internal
energy can not be any greater than the difference between the total collision energy and the \( N_2 \) dissociation energy. For instance, all of the remaining molecules in the \( c_r = 8 \) km/s case had internal energies less than their initial value. The proportion of surviving molecules with internal energy greater than or equal to their initial internal energy increases with increasing relative velocity.

Similarly, Fig. 6.18(b) shows the cumulative distribution of post-dissociation internal energy bin index of the remaining \( N_2 \) in a \( N_2 + N_2 \rightarrow N_2 + 2N \) reaction for various initial bin indices, where \( b_A = b_B = b \) and \( c_r = 8 \) km/s. Again, it is observed that increasing the collision energy leads to a shift of the distribution to higher post-reaction indices. It is also noted that the post-reaction bin index is much more likely to be lower than its initial value than equal to, or greater than its initial value. For these dissociations in which \( c_r = 12 \) km/s, no more than 30% of the remaining \( N_2 \) molecules have initial internal energy greater than, or equal to its initial internal energy value. Rather, the remaining molecule is much more likely to have lost internal energy in the dissociation process. This implies that some transfer of internal energy from the surviving colliding \( N_2 \) to the ultimately dissociated \( N_2 \) is typically a significant contributor to the dissociation process.

For collisions with sufficiently high collision energy, the double dissociation process where \( N_2 + N_2 \rightarrow 4N \) is possible. Figure 6.19(a) shows the MD/QCT-computed \( N_2 + N_2 \rightarrow 4N \) reaction probabilities versus \( \bar{E}_c \). Double dissociation is only possible when total collision energy is greater than \( 2D_e = 460 \) kcal/mol, but Fig. 6.19(a) shows non-zero probabilities for several cases with \( \bar{E}_c \) slightly less than \( 2D_e = 460 \) kcal/mol. Recall that the \( \bar{E}_c \) is the average collision energy in each case. Therefore, although a
given case may have $\bar{E}_c < 2D_e$, it may consist of individual trajectories with sufficient collisional energy to result in a double dissociation reaction. Similar to the single dissociation process, in general, the probability of double dissociation increases with increasing collision energy, but, for a given collision energy, the probability of double dissociation can vary significantly, based on possible differences in the partitioning of energy in the collision. This is observed more clearly in Fig. 6.19(b), where the MD/QCT-computed probability of the double dissociation reaction is shown versus relative velocity for various initial internal energy pairs, where $b_A = b_B = b$. The probability of double dissociation increases with increasing relative velocity and increasing initial internal energy. For high initial internal energy cases ($b \approx 21$) and high relative velocities ($c_r \approx 15$ km/s),
the double dissociation reaction probability is approximately on the same order of magnitude as the single dissociation process shown in Fig. 6.16(b). It is again specifically noted that the highest double dissociation probabilities shown are for the quasi-bound cases \((b_A = b_B = 41)\).

![Graphs](image)

(a) Reaction probability versus \(E_c\) for several \(c_r\) versus relative velocity for several initial internal energy pairs, where \(b_A = b_B = b\)

Fig. 6.19. MD/QCT-computed reactions probabilities for the \(N_2 + N_2 \rightarrow 4N\) process.

Figure 6.20 shows the MD/QCT-computed exchange reaction probability versus relative velocity for various initial internal energy pairs, where \(b_A = b_B = b\). In an exchange reaction, the colliding \(N_2\) molecules trade N atoms resulting in two product \(N_2\) molecules. The probability of an exchange reaction is found to be no greater than 0.1 for all studied collisions. For collisions with low initial internal energies (\(b < 11\),
exchange reaction probability increases with increasing relative velocity for velocities above the threshold energy needed for the exchange reaction. However, for \( b \geq 11 \), there is a relative velocity corresponding to a maximum exchange probability, and exchange probability decreases with increasing relative velocity greater than this relative velocity. This is because collisions with parameters that would lead to exchange reactions at lower relative velocities are more likely to lead to dissociation at higher relative velocities.

Fig. 6.20. MD/QCT computed reaction probabilities versus relative velocity for several initial internal energy pairs for the exchange reaction in which the colliding \( \text{N}_2 \) molecules trade N atoms, where \( b_A = b_B = b \).
6.5.3 Bin-to-Bin Internal Energy Relaxation

Bin-to-bin transition probabilities $P(b_A, b_B, c_r \rightarrow b'_A, b'_B)$, which may be used in a future DSMC implementation, can be determined by dividing the corresponding bin-to-bin cross section, $\sigma(b_A, b_B, c_r \rightarrow b'_A, b'_B)$, by the total collision cross section, as done in Eq. 6.13. Figure 6.21 shows three separate contour plots of bin-to-bin cross sections, where each contour plot has unique initial collision conditions: $b_A$, $b_B$, and $c_r$. In Fig. 6.21(a), where $b_A = 5$ (internal energies ranging from 23-28.75 kcal/mol), $b_B = 20$ (internal energies ranging from 109.25-115 kcal/mol), and $c_r = 5$ km/s, it is observed that the most probable outcome is the elastic process where $b'_A = 5$ and $b'_B = 20$. In general, the bin-to-bin cross sections decrease in size as $|b'_A - b_A|$ or $|b'_B - b_B|$ increases. However, large jumps in internal energy bin values of $|b'_B - b_B| = 5$ and greater are observed, which correspond to internal energy value jumps of 28.75 kcal/mol and greater. Note that, in a collision, the total pre-collision energy determines the possible post-collision internal energy outcomes. In Fig. 6.21(b), $b_B$ is decreased from 20 to 10 (internal energies ranging from 51.75-57.5 kcal/mol), while keeping $b_A = 5$ and $c_r = 5$ km/s from the initial conditions in Fig. 6.21(a), and it is observed that the peak bin-to-bin cross sections shifts to $b'_A = 5$ and $b'_B = 10$. In Fig. 6.21(c), the relative velocity is then increased to 10 km/s, while keeping $b_A = 5$ and $b_B = 10$. The peak bin-to-bin cross section remains at $b'_A = 5$ and $b'_B = 10$, but there is an increased number of post-collision energy bin outcomes, because there is more energy in the collision.
6.5.4 Assigning Post-Collision N$_2$ Internal Energy with a Continuous Internal Energy Spectrum Assumption

The database of MD/QCT-generated bin-to-bin cross sections can be used in DSMC to model internal energy relaxation in N$_2$-N$_2$ collisions. First, the bin-to-bin cross sections are converted to probabilities, $P(b_A, b_B, c_r \rightarrow b'_A, b'_B)$, by dividing each bin-to-bin cross section by the total cross section (given in Section 6.5.1). Then, the probability that a collision is inelastic, in which at least one of the colliders changing its
internal energy bin value, \( P_{inel}(b_A, b_B, c_r) \), is given as

\[
P_{inel}(b_A, b_B, c_r) = \sum_{b'_B = 1}^{46} \sum_{b'_A = 1}^{46} \sum_{b'_B \neq b_B}^{b'_B \neq b_B} P(b_A, b_B, c_r \rightarrow b'_A, b'_B) + \sum_{b'_A = 1}^{46} \sum_{b'_B \neq b_B}^{b'_B \neq b_B} P(b_A, b_B, c_r \rightarrow b'_A, b'_B = b_B) + \sum_{b'_B = 1}^{46} \sum_{b'_A = 1}^{46} P(b_A, b_B, c_r \rightarrow b'_A = b_A, b'_B)
\]

where the first term on the right-hand side of the equation is the total probability that the collision changes both internal energy bin indices \((b'_A \neq b_A, b'_B \neq b_B)\), and the second and third terms are the total probabilities that the collision changes only one of the internal energy bin indices, \((b'_A \neq b_A, b'_B = b_B)\) and \((b'_B \neq b_B, b'_A = b_A)\), respectively.

Consider a \( N_2 - N_2 \) collision with initial total internal energies \( E_{i,A} \) and \( E_{i,B} \) and a relative velocity \( c_r \), giving a total collision energy \( E_c = E_{i,A} + E_{i,B} + 0.5 \mu c_r^2 \). Assuming that the molecular internal energy levels are treated continuously in DSMC, the following procedure outlines the method for using the MD/QCT-generated database of bin-to-bin cross sections.

1. For a selected pair of \( N_2 \) particles, determine the internal energy bin indices of each of the colliding molecules, \( b_A \) and \( b_B \).
2. Determine the probability of an inelastic collision, $P_{inel}(b_A, b_B, c_r)$, by interpolating between the tabulated probabilities at relative velocities $c_r^+$ and $c_r^-$, $P_{inel}(b_A, b_B, c_r^+)$ and $P_{inel}(b_A, b_B, c_r^-)$.

3. Select a random number, $R_1 \in [0, 1]$, and if $R_1 > P_{inel}(b_A, b_B, c_r)$, the collision is elastic and a VHS collision is performed without any change in $N_2$ internal energies. Else, the collision is inelastic, and continue to the next step.

4. The post-collision internal energy bin indices $b'_A$ and $b'_B$ are selected using the algorithm illustrated in Fig. 6.22, where $P(b_A, b_B, c_r \to j, k)$ is determined by interpolating between the tabulated probabilities at relative velocities $c_r^+$ and $c_r^-$, $P(b_A, b_B, c_r^+ \to j, k)$ and $P(b_A, b_B, c_r^- \to j, k)$, and integers $j$ and $k$ are looped through the possible inelastic post-collision bin index $(b'_A, b'_B)$ pairs, i.e. those in which $j \neq b_A$ or $k \neq b_B$. For each $(j, k)$ pair, the probability of the inelastic collision resulting in the $(j, k)$ bin index pair is added to a cumulative probability, $C$. When $R_2 \leq C$, the post-collision bin indices $b'_A$ and $b'_B$ are set to $j$ and $k$, respectively.

5. Determine the post-collision total internal energies, $E'_{i,A}$ and $E'_{i,B}$, using the following equations, where $E_{max}(b)$ and $E_{min}(b)$ define the energy range of bin $b$ (see Table 6.3) and $R_3$ and $R_4$ are random numbers between 0 and 1,

$$E'_{i,A} = R_3 \left[ E_{max}(b'_A) - E_{min}(b'_A) \right] + E_{min}(b'_A)$$

$$E'_{i,B} = R_4 \left[ E_{max}(b'_B) - E_{min}(b'_B) \right] + E_{min}(b'_B).$$

(6.19)
6. The post-collision total internal energies are allocated to the rotational and vibrational modes proportionally according to their respective degrees of freedom, $\zeta_{\text{rot}}$ and $\zeta_{\text{vib}}$,

\[
E'_{\text{rot},A} = \frac{\zeta_{\text{rot}}}{\zeta_{\text{rot}} + \zeta_{\text{vib}}} E'_{i,A}
\]
\[
E'_{\text{rot},B} = \frac{\zeta_{\text{rot}}}{\zeta_{\text{rot}} + \zeta_{\text{vib}}} E'_{i,B}
\]
\[
E'_{\text{vib},A} = \frac{\zeta_{\text{vib}}}{\zeta_{\text{rot}} + \zeta_{\text{vib}}} E'_{i,A}
\]
\[
E'_{\text{vib},B} = \frac{\zeta_{\text{vib}}}{\zeta_{\text{rot}} + \zeta_{\text{vib}}} E'_{i,B},
\]

where $\zeta_{\text{rot}}$ and $\zeta_{\text{vib}}$ are determined from Eqs. 1.9 and 1.10, respectively, with characteristic temperature of vibration $\theta_v = 3371$ K and using a collision-based temperature, $T_{\text{coll}}$, in Eq. 1.10, which is defined as

\[
T_{\text{coll}} = \frac{\pi \mu c_r^2}{8 k_B}.
\]

7. The post-collision relative translational energy, $E'_{t}$, is determined from conservation of energy,

\[
E'_{t} = E_c - E'_{i,A} - E'_{i,B},
\]

and it follows that the post-collision relative velocity, $c_r'$, is given as

\[
c_r' = \sqrt{\frac{2 E'_{t}}{\mu}}.
\]
8. Determine the final velocity of the colliding $N_2$ molecules by randomly selecting directional components of relative velocity, $c'_{r,i}$, where subscript $i$ is the directional index, using the methodology detailed in Section 11.2 of Bird [4]. The final velocities of each $N_2$, $c_{A,i}$ and $c_{B,i}$, are then

$$c_{A,i} = c_{cm,i} - 0.5M_{N_2}c'_{r,i},$$

$$c_{B,i} = c_{cm,i} + 0.5M_{N_2}c'_{r,i},$$

where $c_{cm,i}$ is the velocity of the center of mass of the $N_2$ molecules and $M_{N_2}$ is the $N_2$ mass.

Fig. 6.22. Algorithm for selecting post-collision internal energy bin indices $b'_A$ and $b'_B$ in an inelastic collision using the MD/QCT bin-to-bin internal energy relaxation model.
The preceding algorithm employs the use of the MD/QCT-computed bin-to-bin cross sections to model internal energy exchange in DSMC. The MD/QCT method is accurate for relatively high collision energies (for $c_r \approx 1 \text{ km/s}$), which means that it is ideally suited for high-temperature gases, such as those expected in hypersonic shocks. It is also noted that, because post-collision internal energies are allocated proportionally to the vibrational and rotational modes according to their respective degrees of freedom, vibrational and rotational temperatures are expected to relax at approximately the same rates in cases of strong thermal nonequilibrium.

### 6.5.5 Assigning Post-Collision Rovibrational Levels

When specific, discrete rovibrational levels are modeled in DSMC, a strategy for selecting the rovibrational levels within a given energy bin is needed. In this work, a Maxwell-Boltzmann distribution of the rovibrational levels within an energy bin will be assumed. For a $N_2$ molecule that has a post-collision internal energy bin index $b$, the expected number density of rovibrational level $i$, $n_i$, relative to the total number density of the bin, $\bar{n}_b$, assuming a Maxwell-Boltzmann distribution at internal, or rovibrational temperature $T_{int}$, is

$$\frac{n_i}{\bar{n}_b} = \frac{1}{Q_b(T_{int})} g_i \exp \left( \frac{-E_i}{k_B T_{int}} \right), \quad (6.25)$$

where $Q_b(T_{int})$ is the internal energy partition function within bin $b$ defined as,

$$Q_b(T_{int}) = \sum_{i \in I_b} g_i \exp \left( \frac{-E_i}{k_B T_{int}} \right). \quad (6.26)$$
The post-collision rovibrational level \( i \) can then be selected by random sampling from the distribution of rovibrational levels within bin \( b \) defined by Eq. 6.25. Recall that 
\[
E_i = E(v_i, J_i),
\]
so it then follows that the selected vibrational and rotational levels are \( v_i \) and \( J_i \), respectively. For non-reacting collisions with initial bin indices \( b_A \) and \( b_B \) and a relative velocity of \( c_r \), the post-collision bin indices \( b'_A \) and \( b'_B \) are determined by randomly sampling from the corresponding MD/QCT-generated distribution of bin-to-bin probabilities, \( P(b_A, b_B, c_r \to b'_A, b'_B) \). Then, the rovibrational levels of each molecule are selected by randomly sampling from the Boltzmann distributions of rovibrational levels within their respective energy bins (defined in Eq. 6.25).

Figure 6.23(a) shows the expected distribution of post-collision vibrational \( v' \) levels for non-reacting collisions with varying relative velocities, \( c_r \), for \( b_A = b_B = 1 \) using the DSMC procedure outlined in the previous paragraph. For each relative velocity, 5,000,000 post-collision rovibrational samples are computed. A collision-based temperature is used for the \( T_{int} \) value of Eqs. 6.25 and 6.26. For the \( c_r = 2 \text{ km/s} \) case, only the \( v = 0 \) and \( v = 1 \) levels are populated. This was expected because MD/QCT collisions with \( b_A = b_B = 1 \) and \( c_r = 2 \text{ km/s} \) resulted in post-collision bin indices \( b'_1 \leq 2 \), and the only vibrational levels available in bins 1 and 2 are \( v = 0 \) and \( v = 1 \). As relative velocity increases, higher post-collision energy bins are accessed and, therefore, higher lying vibrational levels become increasingly likely. The corresponding expected distribution of post-collision \( J' \) levels for the same collision conditions are shown in Fig. 6.23(b). In contrast to the smooth \( v' \) distributions, the \( J' \) distributions are relatively discontinuous from level to level due to the nuclear spin degeneracy, which means that even \( J' \) levels are twice as probable as odd levels. Additionally, there appear to be a finite
number of discrete modes in each $J'$ distribution (for $J'$ ranging from 0 to 18, 19 to 36, etc.). These discrete modes are an artifact of the coarse-grain bin model and are more clearly observed for collisions with lower relative velocity in which fewer post-collision energy bins are accessed. For instance, as previously discussed, only post-collision bin indices $b' \leq 2$ are possible for the $c_r = 2$ km/s case. Bin 1 only contains rotational levels ranging from 0 to 18 in the vibrational ground state, bin 2 only contains rotational levels ranging from 0 to 4 in the $v = 1$ state and 19 to 36 in the ground vibrational state, so the distribution shows distinct modes for those respective ranges of $J'$ values. Higher energy bins are accessed as relative velocity increases, which correspondingly allows for population and greater proportion of higher lying rotational levels.

Fig. 6.23. Distribution of post-collision quantum levels for $N_2(b_A) + N_2(b_B)$ with varying relative velocities, $c_r$, and where $b_A = b_B = 1$, assuming a Boltzmann distribution of levels within a bin.
Figure 6.24(a) shows the expected distribution of post-collision \( v' \) levels for non-reacting collisions with varying initial internal energies, where \( c_r = 8 \text{ km/s} \). Again, 5,000,000 post-collision rovibrational samples are computed for each set of initial bin indices, and a collision-based temperature \( T_{int} \approx 42,000 \text{ K} \) is used for the Boltzmann distributions defined in Eqs. 6.25 and 6.26. Bi-modal distributions are observed for the cases where the initial energy bins are greater than unity. The first mode is relatively flat up to a given \( v' \) value, then the distribution decreases with a larger slope for the second mode. It is found that the mid-point of the first mode corresponds to the average vibrational level (shown in Fig. 6.6), \( \bar{v}_b \) of the initial bin indices, \( b \). For instance, \( \bar{v}_{31} = 15.04 \), and the first mode of the distribution for the \( b_A = b_B = 31 \) case is centered at \( v' \approx 15 \) and extends to \( v' \approx 30 \). Similarly, \( \bar{v}_{16} = 6.75 \), and the first mode of the distribution for the \( b_A = b_B = 16 \) case is centered at \( v' \approx 6.5 \) and extends to \( v' \approx 13 \). The corresponding expected distribution of post-collision \( J' \) levels for the same collision conditions of Fig. 6.24(a) are shown in Fig. 6.24(b). With the exception of the \( b_A = b_B = 1 \) case, the \( J' \) follow Boltzmann-like distributions. As the initial internal energies increase, higher lying rotational levels are increasingly probable. The discrete modal behavior of the \( b_A = b_B = 1 \) case is due to the limited number of bins accessed for that low-energy collision, as discussed in the previous paragraph.

### 6.6 Influence of MD/QCT-Based Models on Thermal Nonequilibrium Heat Bath DSMC Calculations

In this section, the effect of implementing the nitrogen MD/QCT chemistry and internal energy relaxation models into DSMC is explored. The MD/QCT-based reaction
Fig. 6.24. Distribution of post-collision quantum levels for $N_2(b_A) + N_2(b_B)$ with varying initial bin indices and relative velocity $c_r = 8 \text{ km/s}$, assuming a Boltzmann distribution of levels within a bin.

probabilities for both the N-N$_2$ (Section 5.5) and N$_2$-N$_2$ (Section 6.5.2) pairs and the N$_2$-N$_2$ continuous internal energy relaxation model (Section 6.5.4) are implemented in the DSMC computational tool, SMILE [87]. Time-dependent thermal nonequilibrium heat bath DSMC simulations were used to determine the explicit expected differences between solutions obtained using the new MD/QCT-based methods and those obtained using the baseline TCE chemistry model and LB internal energy relaxation model.

The computational domain is 2 cm $\times$ 2 cm with specular wall boundary conditions. The number density is initially $6.0 \times 10^{22} \text{ m}^{-3}$ consisting of pure N$_2$. The ratio of real gas particles to DSMC simulated particles is $3.0 \times 10^{14}$, and the timestep is $1 \times 10^{-10} \text{ s}$. The N$_2$ computational particles are initialized with a Boltzmann distribution at a translational temperature $T = 40,000 \text{ K}$. The N$_2$ internal energy is treated
continuously, and initial rotational, $T_{rot}$, and vibrational, $T_{vib}$, temperatures are set to 300 K, thus giving the system a strong degree of initial thermal nonequilibrium. As each simulation progresses, the N$_2$-N$_2$ and N$_2$-N collisions will act to equilibrate the translational and internal temperatures and dissociate N$_2$ molecules. Because the simulations are adiabatic (not isothermal), the endothermic N$_2$ dissociation reactions decrease the energy within the heat bath, thus causing a corresponding decrease in temperature. Only the N$_2$ dissociation reactions via collisions with N or N$_2$ are modeled, meaning that N$_2$ recombination is not considered.

Three separate cases are computed, each with different internal energy relaxation and dissociation models. First, the baseline case is that which employs the TCE model to determine N$_2$ dissociation probabilities and the LB model for internal energy relaxation. This case will be referred to as the (TCE+LB) case. For the LB method, the probability of a collision being rotationally or vibrationally inelastic is the inverse of each respective collision number. The rotational collision number $Z_R$ is determined using the Parker [63] model, with $Z_{R,\infty} = 15.7$ K and $T^* = 80$ K, and the vibrational collision number $Z_V$ is determined using the Millikan-White [64] form with Park [3] high-temperature correction. The second case replaces the TCE model for determining N$_2$ dissociation probabilities with the MD/QCT-generated probabilities, uses the LB model for internal energy relaxation, and will be referred to as the (MD/QCT+LB) case. The third case uses the MD/QCT-generated probabilities of N$_2$ dissociation, replaces the LB model for N$_2$-N$_2$ internal energy relaxation with the MD/QCT-generated bin-to-bin internal energy relaxation model described in Section 6.5.4, and will be referred to as the (MD/QCT+MD/QCT) case. For all three cases, total cross sections are modeled
with the VHS approach with parameters fit to the MD/QCT results for both the N-N$_2$ (Section 5.4) and N$_2$-N$_2$ (Section 6.5.1) pairs and N-N$_2$ inelastic collisions are modeled by the LB approach.

![Diagram](image)

(a) N$_2$ Translational, Rotational, and Vibrational temperatures
(b) N Mole Fraction

Fig. 6.25. Transient thermal and chemical response for a heat bath initially with pure N$_2$ at $T = 40,000$ K and $T_{rot} = T_{vib} = 300$ K.

Figure 6.25(a) shows the transient thermal and chemical response for all three cases. The rotational and translational temperatures of the (TCE+LB) and (MD/QCT+LB) cases equilibrate with each other, but the vibrational temperature does not and lags. The nonequilibraion of the vibrational temperature is because $Z_{vib}$ increases beyond values over 10,000, which means that vibrationally inelastic N$_2$ collisions that would facilitate the equilibration process are less likely. However, when the MD/QCT bin-to-bin internal
energy relaxation model is introduced in the (MD/QCT+MD/QCT) case, the vibrational temperature equilibrates with the rotational and translational temperatures and, as expected, the (MD/QCT+MD/QCT) rotational and vibrational temperatures relax at approximately the same rate and have identical time dependence. The N mole fractions are representative of the number dissociated N\textsubscript{2} molecules and are shown in Fig. 6.25(b).

The (TCE+LB) case initially predicts more N\textsubscript{2} dissociation than the (MD/QCT+LB) and (MD/QCT+MD/QCT) cases because the MD/QCT dissociation probabilities are relatively low for initial N\textsubscript{2} internal energy, whereas the TCE model dissociation probabilities are weakly dependent on initial N\textsubscript{2} internal energy and can thus still have relatively high dissociation probabilities for the high relative collision velocities expected with translational temperatures near 40,000 K. As the internal temperatures increase, the (MD/QCT+LB) and (MD/QCT+MD/QCT) cases dissociate N\textsubscript{2} more rapidly, and eventually dissociate significantly more N\textsubscript{2}, than the (TCE+LB) case. For \( t < \approx 3 \times 10^{-7} \) s, the (MD/QCT+LB) \( T \) is greater than the (MD/QCT+MD/QCT) \( T \), therefore the (MD/QCT+LB) model correspondingly dissociates more N\textsubscript{2} during this time. After \( t < \approx 3 \times 10^{-7} \) s, the \( T \) for the (MD/QCT+LB) and (MD/QCT+MD/QCT) cases are approximately equal. However, because \( T_{vib} \) is greater for the (MD/QCT+MD/QCT) than the (MD/QCT+LB) case, the (MD/QCT+MD/QCT) case begins to dissociate N\textsubscript{2} slightly more rapidly than the (MD/QCT+LB) case, yet not enough to eventually dissociate as much as the (MD/QCT+MD/QCT) case. Because there is more dissociation for the cases with the MD/QCT dissociation probabilities, those cases equilibrate to lower temperatures than the TCE chemistry case.
6.7 State-Specific Vibrational Relaxation and Comparison with FHO Model

An assessment of the accuracy of the well-known analytic FHO vibrational energy relaxation model \[15\] is presented here by a comparison with MD/QCT values, and the assumption that the latter is more accurate, given its use of a more accurate potential. In this section, state-specific vibrational relaxation cross sections and rates will be computed using the MD/QCT method, meaning that rovibrational levels will no longer be grouped into internal energy bins.

In state-specific MD/QCT cases, the initial vibrational and rotational level of each molecule must be specified: \(v_A, v_B, J_A,\) and \(J_B,\) in addition to the relative collision velocity \(c_r.\) In order to determine state-specific relaxation cross sections, the post-collision vibrational and rotational levels \(v'_A, v'_B, J'_A,\) and \(J'_B\) will need to be determined for each trajectory in each case. The following procedure is used in order to determine the post-collision \(v'\) and \(J'\) levels,

1. The post-collision internal energy \(E'_\text{int}\) is the sum of the potential energy and kinetic energy of the molecule relative to the velocity of its center of mass.

2. The magnitude of post-collision angular momentum is computed directly from the coordinates and momenta of the molecule using

\[
|\vec{L}| = \left| \sum_{j=1}^{N} \vec{r}_j \times m_j \vec{c}_j \right|, \tag{6.27}
\]
where \( j \) is the index of each atom of the molecule, and \( \vec{r}_j \) and \( \vec{c}_j \) are the atom’s position and velocity relative to the molecular center of mass, respectively.

3. The angular momentum of a diatomic molecule can be defined by its rotational level, \( J' \), from

\[
L^2 = J'(J' + 1)\hbar^2. \tag{6.28}
\]

However, because \( J' \) must be an integer, the continuous treatment of internal energy in MD/QCT trajectories does not guarantee an exact solution of Eq. 6.28. Therefore, the post-collision rotational quantum number \( J' \) is that which most closely satisfies Eq. 6.28 and is therefore determined such that \( \left| L^2 - J'(J' + 1)\hbar^2 \right| \) is minimized.

4. With \( J' \) determined, \( v' \) is determined such that \( \left| E(v', J') - E_{int}' \right| \) is minimized, where \( E(v', J') \) are the tabulated rovibrational energy levels based on the ReaxFF potential determined from the WKB method.

For the results shown in this section, the post-collision rotational level is neglected, and the focus will merely be on the post-collision vibrational level and, thus, cross sections will be determined for state-specific vibrational relaxation. Therefore, collisions leading to vibrational levels (\( v_A = 0, v_B = 1 \)), for instance, may do so with different post-collision rotational levels, but each are counted equally in the determination of the vibrational relaxation cross sections, probabilities, and rates. The probability of a collision with initial vibrational states \( v_A, v_B \), and collision velocity \( c_r \), resulting in
post-collision vibrational states $v'_A$ and $v'_B$, $P(v_A, v_B, c_r \rightarrow v'_A, v'_B)$ is determined from

$$P(v_A, v_B, c_r \rightarrow v'_A, v'_B) = \frac{N(v_A, v_B, c_r \rightarrow v'_A, v'_B)}{N_T(v_A, v_B, c_r)}, \quad (6.29)$$

where $N(v_A, v_B, c_r \rightarrow v'_A, v'_B)$ is the number of trajectories resulting in post-collision vibrational states $v'_A$ and $v'_B$ and $N_T$ is the total number of trajectories computed. The cross section for that process, $\sigma(v_A, v_B, c_r \rightarrow v'_A, v'_B)$, is then given by

$$\sigma(v_A, v_B, c_r \rightarrow v'_A, v'_B) = P(v_A, v_B, c_r \rightarrow v'_A, v'_B)\pi B_{max}^2. \quad (6.30)$$

In the analytical FHO-CR model [66] internal energy relaxation model, vibrational state-specific transition probabilities and rates are determined analytically using the simple Billing and Fisher [120]. The maximum impact parameter used for the FHO-CR analytical form is 2.5 Å. However, previous MD/QCT results have shown a very strong correlation between maximum impact parameter and predicted post-collision molecular internal energy distributions and, therefore, the expected transition probabilities. To confirm this, the effect of varying $B_{max}$ is shown in Fig. 6.26 on the cross section and probability of the $(1,1) \rightarrow (2,1)$ vibrational transition (where a collision between molecules with initial states $v_A = v_B = 1$ results in post-collision states $v'_A = 2$ and $v'_B = v_B = 1$), with $J_A = J_B = 0$ and a relative velocity $c_r = 6 \text{ km/s}$. The cross section is relatively independent of the maximum impact parameter, ranging between 0.599 and 0.621 Å² for $b_{max}$ ranging from 2.5 to 5 Å, a maximum difference of only 3.4%. However, the probability of transition decreases from 0.031 at $B_{max} = 2.5$ Å to 0.008 at $B_{max} = 5$ Å,
a significant difference. This indicates the importance of the maximum impact parameter on predicted transition probability.

![Graph showing the effect of maximum impact parameter on vibrational transition cross sections and probabilities.]

**Fig. 6.26.** The effect of maximum impact parameter on vibrational transition cross sections and probabilities. \( J_A = J_B = 0 \) and \( c_r = 6 \text{ km/s} \).

The FHO-CR model for internal energy relaxation assumes that the rotational and vibrational relaxation processes are weakly coupled, meaning that initial rotational levels do not significantly affect vibrational state transition probabilities. The effect of initial rotational level \( J \) on MD/QCT vibration transition cross section is examined in Fig. 6.27 by plotting the \((1,1) \rightarrow (2,1)\) vibration transition cross section versus \( J \), where \( J_A = J_B = J \). For all cases, \( v_A = v_B = 1 \) and \( c_r = 6 \text{ km/s} \). The transition cross section increases as \( J \) increases from 0 to 10 because there is more total collision energy, allowing
for more probable transitions. Interestingly, increasing $J$ from 10 to 50, however, does not result in a corresponding increase in transition cross section, which is approximately equal for both initial $J$ values. It was found that de-excitation cross sections were greater, however, for the $J = 50$ case than the $J = 10$ case. When $J$ is increased to 100, the $(1, 1) \rightarrow (2, 1)$ transition cross section again increases due to the increased total collision energy. As $J$ increases to 150, and to 200, the $(1, 1) \rightarrow (2, 1)$ transition cross section decreases, however, as more vibrational transitions become possible with the increased total collision energy. The initial rotational level affect on vibrational transition cross section is seen more clearly by observing the contours of vibrational transition cross sections for various initial $J$ states in Fig. 6.28, where $v_A = v_B = 1$ and $c_r = 8$ km/s in each case displayed. It is clearly observed that higher vibrational levels become increasingly more probable as the initial rotational levels are increased and correspondingly increase the total collision energy.

Vibrational relaxation rate coefficients describing the process where $(v_A, v_B) \rightarrow (v'_A, v'_B)$ are useful to best compare the MD/QCT results to the FHO-CR [66] methodology. For MD/QCT cases in which the impact parameter and molecular orientations are defined in each trajectory using Monte Carlo sampling, the following equation is used to compute the state-specific rate coefficient of a process $s$, $k_s$,

$$
k_s(v_A, v_B) \rightarrow (v'_A, v'_B)(T) = \sum_{J_B = 0}^{J_{max}(v_B)} \sum_{J_A = 0}^{J_{max}(v_A)} \int_0^\infty f(J_A) f(J_B) f(c_r) \sigma(v_A, J_A, v_B, J_B, c_r \rightarrow v'_A, v'_B) c_r dc_r, \quad (6.31)$$
Fig. 6.27. The effect of initial $J$ level on transition cross sections and probabilities, where $J_A = J_B = J$.

where $J_{max}(v)$ is the maximum rotational level possible for vibrational level $v$, and $f$ are the respective probability distribution functions. Equation 6.31 necessitates computing $\sigma_s(v_A, J_A, v_B, J_B, c_r \rightarrow v'_A, v'_B)$ for each of the possible rotational levels for $v_A$, and $v_B$, respectively, and each for enough $c_r$ values to resolve the Boltzmann distribution of relative velocities. Alternatively, to save significant computational cost, Monte Carlo sampling of the rotational levels can be employed and Eq. 6.31 simplifies to

$$k_{(v_A, v_B)\rightarrow(v'_A, v'_B)}(T) = \int_0^\infty f(c_r)\sigma(v_A, v_B, c_r \rightarrow v'_A, v'_B)c_r dc_r.$$  

(6.32)
For the rate coefficients computed in this work, the rotational levels were sampled from a Boltzmann distribution at temperature $T$ that, for a given vibrational level $v$, is

$$\frac{n_{v,J}}{n_v} = \frac{g_J \exp \left( \frac{-E(v,J)}{k_B T} \right)}{Q_v}, \quad (6.33)$$
where $n_{v,J}$ is the number density of molecules in the $(v, J)$ state and $n_v$ is the number density of molecules in the $v$ level, and $Q_v$ is the partition function of the molecules in the $v$ level,

$$Q_v = \sum_{J=0}^{J_{\text{max}}(v)} g_J \exp \left( \frac{-E(v, J)}{k_B T} \right).$$

(6.34)

In Eq. 6.34, $J_{\text{max}}(v)$ is the maximum rotational level for a molecule with vibrational level $v$. For instance, there are 331 $J$ levels for $v = 0$, but only 204 for $v = 20$.

MD/QCT trajectories were computed in order to determine vibrational relaxation rates at six temperatures ranging from 1,000-10,000 K. Each MD/QCT case is defined by the initial vibrational levels $v_A$ and $v_B$, temperature of interest $T$ that controls the sampling of the rotational levels, and relative velocity $c_r$. The remaining computational parameters for these cases are the same as those used in developing the coarse-grain bin model detailed in Section 6.3. The details for selecting the $N_2 J$ levels from a Boltzmann distribution at temperature $T$ are given in Appendix B.6.

Single-quantum change vibrational relaxation rates were computed using the MD/QCT method and compared to the FHO [15] method in Fig. 6.29. The FHO vibrational relaxation model is a predecessor to the newer FHO-CR rovibrational relaxation model. However, like the FHO-CR model, the FHO model depends on the use of the Billing and Fisher intermolecular potential. Because vibrational relaxation rates have not yet been published for the FHO-CR model, relaxation rates can only be compared to the FHO model. There are significant differences observed between the MD/QCT results and the FHO model. The MD/QCT rates are higher than the corresponding FHO rates for lower temperatures (less than $\approx 6,000$ K), particularly for the $v = 1$ case that
exhibits differences of up to several orders of magnitude. However, at high temperatures, the rate coefficients of each model appear to be approaching each other.

![Graph depicting rate coefficients versus temperature](image)

Fig. 6.29. FHO [15] and MD/QCT-computed single-quantum de-excitation rate coefficients versus temperature.

Similarly, the double-quantum change vibrational rate coefficients determined from the MD/QCT results are much higher than the corresponding FHO rate coefficients for temperatures less than ≈ 6,000 K, as shown in Fig. 6.30. Again, both models appear to reach relative agreement as temperature increases to 10,000 K. However, the MD/QCT results predict higher rate coefficients for the $v = 10$ case than the $v = 20$ case at high temperatures, whereas the FHO model predicts higher rate coefficients for the $v = 20$ case for the entire studied temperature range.
The discrepancies between the MD/QCT and analytic FHO vibrational relaxation rates are likely due to a combination of a number of factors previously discussed. The FHO model computes probabilities based on a relatively low maximum impact parameter of 2.5 Å, but it was shown in Fig. 6.26 that the impact parameter can have a significant effect on expected transition probability. The FHO model also assumes an approximate weak coupling of the rotational and vibrational transitions in a collision, but the MD/QCT results of Fig. 6.28 shows that this assumption is unfounded. Finally, the FHO model uses a crude intermolecular potential that departs significantly from the ReaxFF intermolecular potential, shown in Fig. 6.3.

![Fig. 6.30. FHO [15] and MD/QCT-computed double-quantum de-excitation rate coefficients versus temperature.](image)
6.8 Summary

The Molecular Dynamics/Quasi-Classical Trajectories (MD/QCT) method was used to accurately compute collision and reaction cross sections for the N\(_2\)-N\(_2\) collision pair in the ground electronic state for conditions expected in hypersonic shocks. A new potential energy surface was developed using the ReaxFF method and a coarse-grain energy bin model was proposed and implemented. It was found that the total collision cross section did not depend strongly on the initial molecular internal energy and that the dependence on relative velocity followed the commonly observed power-law relationship, enabling the cross sections to be fit to the VHS form. The MD/QCT VHS fit was found to be slightly less than the established DSMC baseline Stallcop VHS curves for hypersonic conditions, but differences were minimal. The MD/QCT-computed reaction probabilities tended to increase with increasing collision velocity and initial molecular internal energies, which is a physical result that the total collision (TCE) model fails to model. For strong nonequilibrium conditions expected in hypersonic shocks, the MD/QCT dissociation probabilities were, in general, less than those determined by the TCE model. However, corresponding MD/QCT equilibrium reaction rates were found to agree well with experimental shock-tube data, thus validating the MD/QCT results. Additionally, the internal energy relaxation process for N\(_2\)-N\(_2\) collisions was examined from the MD/QCT results using a coarse-grain bin model with 46 internal energy bins and computing energy bin-to-bin cross sections. It was found that large jumps in N\(_2\) molecular internal energy are possible for hypervelocity collisions, but the rate of internal energy jumps of bin value ±\(m\) decrease as \(m\) increases, and the rate of internal energy
bin increases of $m$ are approximately equal to the rate of internal energy bin decreases of $m$.

The MD/QCT-based $\text{N}_2$-$\text{N}_2$ collision models were implemented into DSMC and their influence was examined through simulations of a thermal nonequilibrium heat bath approximating hypersonic post-shock conditions. Initially, when there is strong thermal nonequilibrium, the MD/QCT methods predicted less dissociation than the TCE method. As $\text{N}_2$ internal energies equilibrated with the translational mode, the MD/QCT reaction rates surpassed those of the TCE model and, eventually, the MD/QCT chemistry model dissociated more $\text{N}_2$ than the TCE model. The $\text{N}_2$-$\text{N}_2$ internal energy relaxation model was able to equilibrate each of the energy modes, whereas the baseline vibrational relaxation model predicted unrealistically long equilibration times.

State-specific vibrational relaxation rates were found to be significantly different than those predicted by the FHO-CR model. The differences are assumed to be resulting from a number of contributing factors, including: the strong MD/QCT vibrational relaxation dependence on initial rotational levels, the improved intermolecular potential energy surface used in the MD/QCT method, and the effect of using different maximum impact parameters in each model.
Chapter 7

Conclusions

The Direct Simulation Monte Carlo (DSMC) method has frequently been used to model rarefied gases for which the continuum assumption breaks down. It is also advantageous in modeling high-temperature thermochemical nonequilibrium flows because of the relative ease of use of kinetic methods for chemistry and internal energy relaxation. However, the baseline underlying physical models within DSMC are fraught with phenomenological approaches and assumptions and are often based on extrapolations of relatively low-temperature experimental results. The Variable Hard Sphere (VHS) model is used to determine total cross sections as a function of relative collision velocity, but its parameters are based on viscosity data that can only be obtained at relatively low temperatures. The Total Collision Energy (TCE) model is designed to determine reaction probabilities as a function of total collision energy such that it reproduces equilibrium, experimentally-determined reaction rates. However, the degree of nonequilibrium can have a significant effect on reaction rates and, in particular, it has been shown that dissociation is vibrationally-favored, which the TCE model fails to account for. Finally, the Larsen-Borgnakke model is favored for modeling internal energy relaxation within DSMC, but it is also based on the assumption of thermal equilibrium defined by a Boltzmann distribution of energy, can predict unphysically high internal energies greater than the molecule’s dissociation energy and, furthermore, often employs
temperature-dependent probabilities of rotational and vibrational relaxation that have questionable validity at high temperatures.

The Ionian atmosphere and hypersonic shocks in the early stages of spacecraft re-entry are two systems of scientific interest that have been simulated by DSMC with questionable accuracy due to the shortcomings of the baseline methodologies. In this thesis, the Molecular Dynamics/Quasi-Classical Trajectory (MD/QCT) method was used to generate improved collision, chemistry, and internal energy relaxation models for the SO$_2$-O collision pair that is critical for Ionian atmosphere interactions with the Jovian plasma torus and the N-N$_2$ and N$_2$-N$_2$ pairs that are relevant in hypersonic shocks.

For the SO$_2$-O pair, a new potential energy surface was developed using a ReaxFF fit to ab initio calculations. The MD/QCT total cross sections were found to be significantly higher than those predicted by the baseline Bird/Ozawa VHS parameters. Dissociation of SO$_2$ to SO is the dominant reactive process, even when the total collision energy is high enough to enable atomization. While the MD/QCT reaction cross sections tended to increase towards unity with increasing relative velocity, as expected, the baseline TCE probabilities could be unphysically above unity. The collision and chemistry models derived in MD/QCT were implemented into DSMC, including 1D simulations of the Ionian atmosphere. Compared to results obtained using the baseline models, these MD/QCT models predicted approximately half the SO$_2$ dissociation, a plasma-heating induced temperature rise further from the Ionian surface, and a decreased particle escape rate. Post-collision SO$_2$ and post-reaction SO internal energy distributions were also determined from the trajectory results, which were used in a new model to determine internal energies resulting from SO$_2$-O collisions in DSMC. The new MD/QCT
internal energy model does not rely on phenomenological assumptions and prevents the possibility of unphysical post-collision internal energies. However, in thermal nonequilibrium heat bath DSMC cases with the new models, the equilibrium temperatures were relatively unaffected due to the continued influence of the baseline model on all other collision pairs in the system.

For the N-N$_2$ collision pair, the potential energy surface developed by Jaffe et al. [106] was used to determine total collision cross sections and well-resolved dissociation probabilities in MD/QCT specifically for use in DSMC. The MD/QCT-derived total cross sections agreed well with established baseline VHS parameters, but were slightly greater than the those determined using the baseline Bird/Ozawa VHS parameters. MD/QCT dissociation probabilities were much more dependent on initial N$_2$ internal energy and relative velocity than the TCE model, and tended towards unity with increasing collision energy, unlike the TCE probabilities. A constant rotational relaxation number of $Z_R = 2.5$ was derived from the state-to-state cross section database of Jaffe et al. [53], which was significantly lower than the Parker [63] model at high temperatures, which had previously been known to under-predict rotational relaxation rate in strong shocks. The MD/QCT models had a significant effect on 2D axisymmetric flows over a blunt body. The total cross sections led to a slightly narrower shock profile, the chemistry model gave increased N$_2$ dissociation that, combined with the higher rotational temperatures given by the constant rotational relaxation collision number, led to a corresponding decrease in translational temperature.

MD/QCT studies on the N$_2$-N$_2$ collision pair employed the use of a new potential energy surface that was a ReaxFF fit to the recently computed \textit{ab initio} dataset
of Paukku et al. [13]. Again, the total cross sections agreed relatively well with the established baseline cross sections. However, the MD/QCT dissociation probabilities were generally less than those predicted by the TCE model for strong nonequilibrium conditions and were also more strongly dependent on relative velocity and initial internal energies. The internal energy relaxation process was described using a new bin-to-bin approach in which rovibrational levels were grouped into a smaller number of internal energy bins. In a DSMC thermal nonequilibrium heat bath case, the MD/QCT-based $N_2-N_2$ models initially predicted less dissociation than the TCE method but, as $N_2$ internal energies increased, the MD/QCT case predicting an increasing rate of dissociation such that the MD/QCT case eventually dissociated more $N_2$ than the TCE model. Furthermore, the bin-to-bin internal energy relaxation model was able to equilibrate each of the energy modes, whereas the baseline vibrational relaxation model predicted unrealistically long equilibration times. Several state-specific vibrational relaxation rates were then computed with the MD/QCT method and compared to the increasingly popular FHO-CR [66] method. Significant differences were found between the excitation rates, which is explained by the more advanced potential energy surface used in MD/QCT cases, the strong MD/QCT vibrational relaxation dependence on initial rotational levels that is ignored by the FHO-CR model, and the effect of using difference maximum impact parameters in each model.

The MD/QCT-based DSMC models developed in this thesis represent an important contribution to the modeling of nonequilibrium rarefied gases. The existing baseline methodologies for collision cross sections, reaction probabilities, and internal energy relaxation were each permeated with low-order and/or phenomenological assumptions and
often employed species-specific parameters that were determined from extrapolations of relatively low-temperature data. These models were therefore generally unreliable and, worse, produced clearly unphysical results. In contrast, by using MD/QCT results that are based on trajectories computed with accurate potential energy surfaces, DSMC models can be created that are not only physical, but based on first principles. Coupling the resulting collision, chemistry, and internal energy relaxation MD/QCT models together in DSMC gives a consistent, accurate approach for particle interactions based on rigorous physical models and devoid of low-order assumptions. The promising numerical methods presented are well-suited to guide further MD/QCT studies in order to better model other collision pairs important in modeling nonequilibrium rarefied gases.
Appendix A

The Runge Kutta Method for Solving Hamilton’s Equations

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

\[ \dot{p}_{i,j} = -\frac{\partial V}{\partial r_{i,j}} \]  
\[ \dot{r}_{i,j} = \frac{p_{i,j}}{M_i} \]  

where \( V \) is the system potential, \( p \) is atomic momentum, \( r \) is atomic position, \( M \) is atomic mass, \( i \) is the atomic index, and \( j \) is the direction index. Hamilton’s equations are solved using a fourth-order Runge-Kutta method,

\[ p_{i,j}^{n+1} = p_{i,j}^n + \frac{1}{6} \left( k_{1,i,j}^n + 2k_{2,i,j}^n + 2k_{3,i,j}^n + k_{4,i,j}^n \right) \]  
\[ r_{i,j}^{n+1} = r_{i,j}^n + \frac{1}{6} \left( l_{1,i,j}^n + 2l_{2,i,j}^n + 2l_{3,i,j}^n + l_{4,i,j}^n \right) \]
\[ k^n_{1,i,j} = -\Delta t \left( \frac{\partial V}{\partial r_{i,j}} \right) \bigg|_{r^n_{i,j}} \]

\[ k^n_{2,i,j} = -\Delta t \left( \frac{\partial V}{\partial r_{i,j}} \right) \bigg|_{r^n_{i,j}+m^n_{1,i,j}/2} \]

\[ k^n_{3,i,j} = -\Delta t \left( \frac{\partial V}{\partial r_{i,j}} \right) \bigg|_{r^n_{i,j}+m^n_{2,i,j}/2} \]

\[ k^n_{4,i,j} = -\Delta t \left( \frac{\partial V}{\partial r_{i,j}} \right) \bigg|_{r^n_{i,j}+m^n_{3,i,j}} \]

\[ (A.4) \]

\[ k^n_{1,i,j} = \Delta t \left( \frac{p^n_{i,j}}{m_i} \right) \]

\[ k^n_{2,i,j} = \Delta t \left( \frac{p^n_{i,j} + k^n_{1,i,j}/2}{m_i} \right) \]

\[ k^n_{3,i,j} = \Delta t \left( \frac{p^n_{i,j} k^n_{2,i,j}/2}{m_i} \right) \]

\[ k^n_{4,i,j} = \Delta t \left( \frac{p^n_{i,j} k^n_{3,i,j}}{m_i} \right) \]

\[ (A.5) \]

where \( n \) is the time index.
Appendix B

Generation of MD/QCT Initial Conditions

Each case of an MD/QCT study in this thesis is defined by a relative collision velocity and definition of initial molecular internal energy. These cases consist of a large number of trajectories that each have unique combinations of impact parameters and molecular orientations and, possibly, varied internal energy partitions. These trajectory parameters define the initial atomic coordinates and momenta. This appendix details the process for selecting the trajectory parameters for each case in this thesis.

B.1 Impact Parameter Sampling

The impact parameter is chosen from a probability distribution of [123]

\[ P(B) dB = \frac{2\pi B dB}{\pi B_{\text{max}}^2} \]  \hspace{1cm} (B.1)

where \( B_{\text{max}} \) is the maximum allowed impact parameter. This is a strategically chosen parameter that is large enough to include all significant trajectories for which energy exchange can occur, yet not so large so as to compute uninteresting trajectories for which there is no interaction. The impact parameter is selected with

\[ B = B_{\text{max}} \sqrt{R_f}, \]  \hspace{1cm} (B.2)
where $R_f$ is a random number selected from a uniform distribution between 0 and 1.

**B.2 Molecular Orientation Sampling**

The initial orientation of MD/QCT molecules with respect to an initial baseline orientation is selected by crude Monte Carlo sampling [123]. The SO$_2$ baseline molecular orientation is in the x-y plane, with the center of mass placed at the origin and the S atom confined to the y-axis. The N$_2$ baseline molecular orientation had its center of mass lying on the x-axis with the x-axis perpendicular to the N-N bond. The molecular orientations were then determined by three successive Eulerian rotations, in which the molecule is first rotated $\phi$ about the z-axis, then rotated $\theta$ about the x'-axis, then finally rotated $\psi$ about the z'-axis. This rotation scheme is illustrated in Fig. B.1. The Euler angles are determined by

$$
\phi = 2\pi R_1, \quad \theta = 2\pi R_2, \quad \psi = 2\pi R_3,
$$

(B.3)

where $R_i$ are random numbers uniformly distributed between 0 and 1.

**B.3 Determining SO$_2$ Geometry and Interatomic Momenta Through Microcanonical Sampling**

In the SO$_2$-O MD/QCT studies of Chapters 2 and 4, each case was defined by a relative velocity and initial SO$_2$ internal energy, $E_i$. The partition of that internal energy was not specified, so the microcanonical sampling method was used to determine the partitioning and, thus, initial coordinates and momenta of the SO$_2$ atoms for each
trajectory. The SO$_2$ molecular geometry is uniquely defined by three parameters: bond lengths $r_{12}$ and $r_{13}$ and bond angle $\alpha$. The probability of a given SO$_2$ geometry, with specified internal energy $E_i$ is

$$W \propto r_{12}^2 r_{13}^2 \sin \alpha [E_i - V(r_{12}, r_{13}, \alpha)]^2,$$

(B.4)

where $V$ is the molecular potential of the molecular geometry, and $E_i \geq V$. Equation B.4 is evaluated for internuclear distances $r_{12}$, $r_{13}$ varying from 1.15 Å to 3.5 Å for the SO$_2$ molecule and bond angle $\alpha$ varying from 0 to $\pi$ in order to determine $W_{\text{max}}$. These internuclear distances are chosen such that the full range of possible SO$_2$ bond lengths are considered.

With the maximum weighting function $W_{\text{max}}$ determined, bond lengths and angles are chosen randomly, and $W$ is computed again for the corresponding geometry.
Then, a standard acceptance-rejection method is used. If a random number $R_f$ (uniformly distributed between 0 and 1) is less than the $W/W_{max}$ ratio, then the geometry is accepted, else a new geometry is generated and the process repeats.

With the SO$_2$ geometry determined, atomic momenta are sampled from a normal distribution such that the SO$_2$ center of mass velocity is zero, and total energy is conserved. This is done by first randomly selecting momenta coordinates with

$$p_{ij} = \sqrt{m_i R},$$

(B.5)

where $R$ is a pseudorandom number distributed according to the standard normal density function. Then, the center of mass velocity as determined by this form is subtracted, and the temporary total kinetic energy $E_{k,tmp}$ is computed. The atomic momenta are then scaled by the factor $\sqrt{E_k/E_{k,tmp}}$, where $E_k$ is the kinetic energy needed to conserve total energy, $E_k = E_i - V(r_{12}, r_{13}, \alpha)$.

B.4 Determining N$_2$ Bond Length and Interatomic Momenta Through Microcanonical Sampling

Similar to the SO$_2$-O pair studied in this thesis, each N-N$_2$ MD/QCT case in Chapter 5 was defined by a relative velocity and initial N$_2$ internal energy, $E_i$. Again, the partition of that internal energy was not specified, so the microcanonical sampling method was used to determine the partitioning. Assuming a harmonic oscillator, [125]

$$W \propto [E_i - V(r_{12})]^\frac{1}{2},$$

(B.6)
where $V$ is the molecular potential of the molecular geometry, and $E_i \geq V$. This equation is evaluated for internuclear distances $r_{12}$ varied by $4.85 \times 10^{-5} \text{ Å}$ from $0.15 \text{ Å}$ to $5.0 \text{ Å}$ to determine $W_{\text{max}}$. This range ensures that the full range of possible N$_2$ bond lengths are considered.

With maximum weighting function $W_{\text{max}}$ determined, a bond length is chosen randomly for each trajectory within a case, and $W$ is computed again for the respective geometry. Then, a standard acceptance-rejection method is used. If a random number $R_f$ (uniformly distributed between 0 and 1) is less than the $W/W_{\text{max}}$ ratio, then the geometry is accepted, else a new geometry is generated and the process repeats. The atomic momenta are then determined in the same manner as done for SO$_2$ in Appendix B.3.

### B.5 Selecting Initial N$_2$ Bond Length and Interatomic Momenta for Specific $(v, J)$ Levels

In the N$_2$-N$_2$ MD/QCT studies of Chapter 6, each trajectory was defined by the initial rovibrational $(v, J)$ levels of each N$_2$ molecule and a relative velocity. Each $(v, J)$ level determined by the WKB method for the ReaxFF potential had corresponding vibrational turning points $r_+(v, J)$ and $r_-(v, J)$ (see Appendix C), which correspond to the maximum and minimum bond lengths for that given rovibrational level, respectively. The initial bond length, $r_{12}$, was thus determined from,

$$r_{12} = (r_+(v, J) - r_-(v, J)) R_f + r_-(v, J),$$  \hspace{1cm} (B.7)
where $R_f$ is a random number uniformly distributed between 0 and 1. Using a rigid rotor model for rotational energy, the rotational energy is

$$E_{\text{rot}}(J) = J(J + 1)\theta_r k_B,$$  \hspace{1cm} (B.8)

where $\theta_r$ is the characteristic temperature of rotation, assumed to be 2.87 K for the N$_2$ molecule. The rotational energy is imparted on the N$_2$ molecule with axis of rotation perpendicular to the x-y plane. The kinetic energy in the vibrational mode, $E_{k,\text{vib}}$, is then determined from conservation of energy,

$$E_{k,\text{vib}} = E(v, J) - V(r_{12}) - E_{\text{rot}}(J),$$  \hspace{1cm} (B.9)

which is used to determine the axial speed of the N atoms relative to the center of mass,

$$\dot{r} = \frac{2E_{k,\text{vib}}}{\mu_{N-N}}.$$  \hspace{1cm} (B.10)

This axial speed is added the N$_2$ molecule with orientation (stretch or compression) randomly selected.

### B.6 Selecting N$_2$ J Levels from a Boltzmann Distribution

The procedure for determining the initial $J$ levels, sampled from a Boltzmann distribution at equilibrium temperature $T$ and with $v$ pre-determined, is outlined. The N$_2$ rotational energy is assumed to be in the rigid rotor form (Eq. B.8). The degeneracy of each level of a molecule modeled by a rigid rotor is $2J + 1$, so the probability density
function is then

\[ f(J) \propto (2J + 1) \exp \left[ -J(J + 1)\theta_r/T \right]. \tag{B.11} \]

The above equation is maximized for

\[ J^* = \frac{1}{2} - \frac{1}{2} \sqrt{\frac{2T}{\theta_r}}. \tag{B.12} \]

The acceptance-rejection method for determining the \( J \) states are as follows:

1. Randomly select \( J \) using

\[ J = \text{INT} \left[ (1 + J_{\text{max}}(v))R_{f1} \right], \tag{B.13} \]

where \( J_{\text{max}}(v) \) is the maximum rotational level for a molecule with vibrational level \( v \) and \( R_{f1} \) is a random number uniformly distributed between 0 and 1. Using the ReaxFF potential, the maximum \( J \) level is a function of the corresponding \( v \) level of the molecule. For example, there are 331 \( J \) levels for \( v = 0 \) but only 204 for \( v = 20 \).

2. Accept \( J \) if \( f(J)/f(J^*) > R_{f2} \), where \( R_{f2} \) is a random number uniformly distributed between 0 and 1.

3. If the value of \( J \) is not accepted, and thus rejected, return to step 1.

Figure B.2 shows the corresponding distribution function of rotational levels \( J \) for various temperatures, as determined using the methodology described above in the MD/QCT code, compared to the expected Boltzmann distribution. It is clearly seen that
the acceptance-rejection method accurately obtains initial rotational levels representative of an equilibrium Boltzmann distribution, assuming a rigid rotor model.

Fig. B.2. Probability distribution function of initial rotational level $J$ in MD/QCT using 40,000 samples compared to expected Boltzmann distribution, for various equilibrium temperatures $T$. 
Appendix C

The WKB Methodology for Determining \((v, J)\) Levels

The following relation defines the rovibrational energy levels \(E(v, J)\) according to the WKB method,

\[
\frac{1}{\hbar} \int_{r_-}^{r_+} \left[ 2\mu(E(v, J) - U(r)) \right]^{1/2} \, dr = \pi \left( v + \frac{1}{2} \right),
\]

(C.1)

where \(r_-\) and \(r_+\) are the inner and outer vibrational turning points, respectively, \(\mu\) is the reduced mass of the N-N atom pair, and \(U(r)\) can be written as the sum of two terms \(U(r) = V(r) + E_{rot}\), where \(V(r)\) is the \(\text{N}_2\) potential computed with no rotation \((J = 0)\) at radius \(r\), and \(E_{rot}\) is the rotational energy, defined in the rigid rotator convention

\[
E_{rot} = \frac{\hbar^2 J(J + 1)}{2\mu r^2}.
\]

(C.2)

Then, re-writing C.1,

\[
\frac{1}{\hbar} \int_{r_-}^{r_+} \left[ 2\mu(E(v, J) - V(r)) - \frac{\hbar^2 J(J + 1)}{r^2} \right]^{1/2} \, dr = \pi \left( v + \frac{1}{2} \right).
\]

(C.3)

To determine \(E(v, J)\), the following simple iterative bisection procedure is followed, where subscripts \(a\), \(b\), and \(c\) represent guesses in each iteration:
1. Record $V(r)$ for many $r$ values. In this work, 50,000 datapoints are recorded for $r$ ranging from 0.8 to 2.566 Å.

2. For the first iteration, define initial guesses $E(v, J)_a = \frac{\hbar^2 J(J+1)}{2\mu r^2}$, $E(v, J)_b = 500$ kcal/mol

3. $E(v, J)_c = (E(v, J)_a + E(v, J)_b)/2$

4. Determine turning points $r_-$ and $r_+$ for each $E(v, J)_j$ guess, where $j$ is a, b, and c, using

   \[ E(v, J)_j - V(r_{+/-}) - \frac{\hbar^2 J(J+1)}{2\mu r^2_{+/-}} = 0 \]  

(C.4)

5. Determine $f(E(v, J)_j)$ for each $E(v, J)_j$, where

   \[ f(E(v, J)_j) = \frac{1}{\hbar} \int_{r_{-}}^{r_{+}} \left[ 2\mu (E(v, J)_j - U(r)) - \frac{\hbar^2 J(J+1)}{r^2} \right]^{1/2} dr - \pi \left( v + \frac{1}{2} \right) \]  

(C.5)

6. If $f(E(v, J)_a)f(E(v, J)_c) > 0$, then $E(v, J)_a = E(v, J)_c$, or else, $E(v, J)_b = E(v, J)_c$.

7. If $|E(v, J)_a - E(v, J)_b| < \varepsilon_E$, then $E(v, J) = E(v, J)_b$ and $f(E(v, J)_c) < \varepsilon_f$, else return to step 3. In this work, $\varepsilon_E = 0.0001$ kcal/mol, and $\varepsilon_f = 0.005 (\pi(v+1/2))$. 

Appendix D

MD/QCT Numerical Parameter Sensitivity

D.1 N-N\textsubscript{2} System

Accuracy of collision and chemistry cross sections as determined from the MD/QCT method are dependent on a number of computational parameters. First, the collider must initially be placed a large enough distance from the target molecule such that there are no initial collider-target interactions, yet not so large that unnecessary computational time is needed to move the collider near the target. For this study, an initial distance of 10 Å is used.

Next, each individual trajectory must have a timestep such that inter-molecular forces are adequately resolved in the temporal domain. Typically, this means that both the collider-target interaction is well resolved, and any molecular internal modes are well resolved. The vibrational frequency of the target N\textsubscript{2} molecule is $\omega_e = 2358.6$ cm\textsuperscript{-1}, corresponding to a period of oscillation of $(\omega_e)^{-1} = 14.14$ fs \cite{82}. If twenty temporal data points are desired for each vibrational oscillation, a timestep $\Delta t < 0.71$ fs is required.

The highest velocity of interest $c_{r,max}$ in the N-N\textsubscript{2} computations is 17.59 km/s. If ten temporal data points are desired for every 1 Å of collider travel in order to resolve the collider-target interaction, a timestep $\Delta t < (10c_{r,max})^{-1} = 0.57$ fs is required. Therefore, the collider-target interaction is the limiting factor, and a timestep of $\Delta t$ of 0.5 fs is used. Table D.1 shows a sample collision and reaction cross section ($N + N_2 \rightarrow 3N$)
computation using timesteps of 0.5 fs and 0.05 fs, respectively. It is noted that the increased resolution of the 0.05 fs timestep does not significantly alter the resulting cross section computations. Therefore, the 0.5 fs timestep is deemed sufficient.

Table D.1. Timestep sensitivity. \( E_{i,N_2} = 9.0 \times 10^{-19} \) J, \( c_r = 17.59 \) km/s, \( B_{max} = 7 \) Å, 20000 trajectories, \( r_{max} = 10 \) Å

<table>
<thead>
<tr>
<th></th>
<th>( \Delta t = 0.5 ) fs</th>
<th>( \Delta t = 0.05 ) fs</th>
<th>Relative error</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \sigma_{MD,VHS} [\text{Å}^2] )</td>
<td>5.035</td>
<td>5.032</td>
<td>0.0006</td>
</tr>
<tr>
<td>( \sigma_{r,N+N_2 \rightarrow 3N} [\text{Å}^2] )</td>
<td>3.163</td>
<td>3.171</td>
<td>0.0025</td>
</tr>
</tbody>
</table>

The number of timesteps necessary for each trajectory is dependent on the initial collider velocity and the timestep. It is desired that the collider is at least 10 Å away from the target upon completion of the simulation, meaning that the collider must move approximately 20 Å. This allows for adequate collider-target interaction, clear determination of post-collision internal energies, and definition of possible dissociation reaction events. For \( c_r \geq 2.54 \) km/s, this is ensured by using 2000 timesteps per trajectory. For the lowest relative velocity of 0.8031 km/s, at least 4939 timesteps are necessary, so for \( c_r < 2.54 \) km/s, 5000 timesteps per trajectory are used.

Proper selection of the initial collider-target distance, timestep, and number of timesteps ensures that each individual trajectory is accurately computed. Computing an adequate number of sampled trajectories, and sampling impact parameters between 0.0 Å up to a well-chosen maximum impact parameter \( B_{max} \) ensure that the resulting
cross section computations are statistically sound. It is found, through inspection, that a maximum impact parameter of 7 Å is large enough to include all possible collider-target interactions, yet not so large that an unnecessary number of insignificant trajectories are computed. Finally, the number of computed trajectories for each case is needed. Table D.2 shows the computed collision cross section for a given case, as determined from running various numbers of trajectories \( N_T \). It is found that there is agreement to within 5\% for all computations presented. However, 20,000 trajectories are chosen for each case in order to give a reaction cross section resolution of \( \pi B_{max}^2 / N_T = 0.008 \text{ Å}^2 \).

<table>
<thead>
<tr>
<th>Trajectories</th>
<th>( \sigma_{MD,VHS} ) [Å²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5k</td>
<td>19.28</td>
</tr>
<tr>
<td>10k</td>
<td>19.68</td>
</tr>
<tr>
<td>20k</td>
<td>19.30</td>
</tr>
<tr>
<td>30k</td>
<td>19.40</td>
</tr>
<tr>
<td>40k</td>
<td>19.24</td>
</tr>
<tr>
<td>60k</td>
<td>19.18</td>
</tr>
<tr>
<td>80k</td>
<td>19.26</td>
</tr>
</tbody>
</table>
D.2 \textit{N}_2-\textit{N}_2 \text{ System}

A set of optimal computational parameters must be determined for the \textit{N}_2-\textit{N}_2 MD/QCT collisions such that cross sections are converged yet computational cost is minimized.

To select the initial collider-target distance, the minimized energy, $E_{\text{min}}(d)$, for various collider-target distances, $d$, was computed. An initial collider-target distance just large enough to ensure no collider-target intermolecular forces are present is desired. It was found that, for $d < 8$ Å, $E_{\text{min}}(d = \infty) - E_{\text{min}}(d) \geq 2 \times 10^{-4}$ kcal/mol, but $E_{\text{min}}(d = \infty) - E_{\text{min}}(d = 10) = 2 \times 10^{-12}$ kcal/mol. Therefore, an initial collider-target distance of 10 Å is used for all cases.

As detailed in Appendix D.1, a timestep of $\Delta t = 0.50$ fs should be sufficient to resolve \textit{N}_2 vibrational oscillations and the collider-target interactions. However, for $c_r = 20$ km/s, it was found that the $\Delta t = 0.5$ fs test case did not sufficiently capture enough exchange reactions that cases with finer timesteps did. It was found, instead, that the total cross section, all reaction cross sections, and the average deflection angle for the $\Delta t = 0.25$ fs case agreed to within 1% of the corresponding values for a $\Delta t = 0.01$ fs case. With $\Delta t = 0.25$ fs, 20 temporal datapoints were resolved for every 1 Å of collider travel. Therefore, it was determined that each case will need 20 temporal data points for every 1 Å of collider travel. The minimum timestep used was 0.25 fs (for high velocity cases), and the maximum timestep was 0.50 fs (for the lowest velocity cases).

Next, the number of timesteps per trajectory were determined, which can also be thought of as the estimated post-collision distance between the collider and target.
at simulation completion and/or the estimated number of post-collision N\textsubscript{2} oscillations. Cross section results for cases with 1200, 1000, 800, 700, and 600 timesteps agreed to within 1\% in a test case with \(c_r = 20\) km/s. Cases with 500 and 400 timesteps did not agree as well, but were still within 4\% of the converged results. Therefore, 600 timesteps for this particular case were deemed sufficient, which corresponded to an estimated post-collision collider-target distance of 20 Å at simulation completion and 7.1 N\textsubscript{2} post-collision oscillations. Therefore, for all cases, the number of timesteps are specified such that there is a post-collision collider-target distance of 15 Å and 7 post-collision N\textsubscript{2} oscillations at the end of each trajectory.

The number of trajectories computed for each case should be enough to obtain converged cross sections and obtain well-resolved deflection angle distributions (and, thus, post-collision internal energy distributions). Again, using a \(c_r = 20\) km/s test case with \(B_{max} = 5\) Å, it was found that results for cases 40,000, 20,000, and 15,000 trajectories each agreed to within 3\%. The 10,000, 5,000, and 1,000 trajectory cases saw larger deviations. The 15,000 trajectory case also gave a sufficient 1106 qualifying “collision” trajectories for use in resolving post-collision deflection angle and internal energy distributions. With \(B_{max} = 5\) Å, this corresponded to a trajectory density of 191 Å\textsuperscript{-2}, so a trajectory density of 200 Å\textsuperscript{-2} is desired for each case.

Lastly, the effect of the maximum impact parameter was tested, while keeping the trajectory density of 200 Å\textsuperscript{-2} for each case. It was found that cases with impact parameters ranging from 4 to 8 Å all had cross section and average deflection angles agreed to within 3\%. These findings were confirmed for cases with \(c_r = 12, 7, \) and 2 km/s. Therefore, for all MD/QCT cases, a maximum impact parameter of 4.0 Å was
used. In keeping the trajectory density of 200 Å$^{-2}$, each case therefore consisted of 10,000 trajectories.

In summary, the initial collider-target distance was 10 Å for each trajectory, and each case consisted of 10,000 trajectories with a maximum impact parameter of 4.0 Å. The timestep and number of timesteps were dependent on the relative velocity, ensuring that the collider-target interaction and vibrational motions were well resolved and that enough timesteps were computed for a post-collision collider-target distance of 15 Å at the end of each trajectory. The specific timesteps and number of timesteps used for each studied relative velocities in the bin model MD/QCT studies of Chapter 6 are listed in Table D.3.

Table D.3. $\text{N}_2$-$\text{N}_2$ MD/QCT numerical parameters dependent on relative velocity, $c_r$.

<table>
<thead>
<tr>
<th>$c_r$ [km/s]</th>
<th>$\Delta t$ [fs]</th>
<th>Timesteps</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.50</td>
<td>5000</td>
</tr>
<tr>
<td>2</td>
<td>0.50</td>
<td>2500</td>
</tr>
<tr>
<td>3</td>
<td>0.50</td>
<td>1700</td>
</tr>
<tr>
<td>4</td>
<td>0.50</td>
<td>1250</td>
</tr>
<tr>
<td>5</td>
<td>0.50</td>
<td>1000</td>
</tr>
<tr>
<td>6</td>
<td>0.50</td>
<td>800</td>
</tr>
<tr>
<td>8</td>
<td>0.50</td>
<td>625</td>
</tr>
<tr>
<td>10</td>
<td>0.40</td>
<td>670</td>
</tr>
<tr>
<td>12</td>
<td>0.40</td>
<td>450</td>
</tr>
<tr>
<td>15</td>
<td>0.25</td>
<td>500</td>
</tr>
<tr>
<td>20</td>
<td>0.25</td>
<td>400</td>
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</table>
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