INVESTIGATION OF AEROTHERMODYNAMIC AND CHEMICAL KINETIC MODELS FOR HIGH-SPEED NONEQUILIBRIUM FLOWS

by

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To my beloved family.

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LIST OF SYMBOLS

M	Mach	number

- ho density, kg/m³
- ρ_s species density, kg/m³
- Y_s species mass fraction
- $M_{w,s}$ species molecular weight, kg/kmol
- P static pressure, pa
- R_u universal gas constant (8.31434 × 10³ J/(kmol· K))
- R gas constant, J/(kg · K)
- N_A Avogadro's constant (6.0221409 × 10²⁶ # of particles per kmol)
- k_b Boltzmann's constant ($k_b = 1.38064852 \times 10^{-23} \text{ J/K}$)
- δ_{ij} Kronecker delta function
- T_t translational temperature, K
- T_r rotational temperature, K
- T_{tr} translational-rotational temperature, K
- T_v vibrational temperature, K
- \bar{c} mean thermal speed, m/s

ABSTRACT

High speed flow problems of practical interest require a solution of nonequilibrium aerothermochemistry to accurately predict important flow phenomena including surface heat transfer and stresses. As a majority of these flow problems are in the continuum regime, Computational Fluid Dynamics (CFD) is a useful tool for flow modeling. This work presents the development of a nonequilibrium add-on solver to *ANSYS Fluent* utilizing user-definedfunctions to model salient aspects of nonequilibrium flow in air. The developed solver was verified for several benchmark nonequilibrium flow problems and compared with the available experimental data and other nonequilibrium flow simulations.

The rate of dissociation behind a strong shock in thermochemical nonequilibrium depends on the vibrational excitation of molecules. The Macheret-Fridman (MF) classical impulsive model provides analytical expressions for nonequilibrium dissociation rates. The original form of the model was limited to the dissociation of homonuclear molecules. In this work, a general form of the MF model has been derived and present macroscopic rates applicable for modeling dissociation in CFD. Additionally, some improvements to the prediction of mean energy removed in dissociation in the MF-CFD model has been proposed based on the comparisons with available QCT data. In general, the results from the MF-CFD model upon investigating numerous nonequilibrium flows are promising and the model shows a possibility of becoming the standard tool for investigating nonequilibrium flows in CFD.

The aerodynamic deorbit experiment (ADE) CubeSat has dragsail to accompany accelerated deorbiting of a CubeSat post-mission. A good estimation of the aerothermal load on a reentry CubeSat is paramount to ensure a predictable reentry. This study investigates the aerothermal load on an ADE CubeSat using the direct simulation Monte Carlo (DSMC) methods and Navier-Stokes-Fourier continuum based methods with slip boundary conditions. The aerothermal load on an ADE CubeSat at 90 km altitude from the DSMC and continuum methods were consistent with each other. The continuum breakdown at a higher altitude of 95 km resulted in a strong disagreement between the continuum and DSMC solutions. Overall, the continuum methods could offer a considerable computational cost saving to the DSMC methods in predicting aerothermal load on an ADE CubeSat at low altitudes.

1. INTRODUCTION

Thermodynamic and chemical equilibrium is reached through molecular collisions. The amount of time that is required to achieve a thermal equilibrium through collisions is known as the thermal relaxation time. In a high speed flow, usually in the presence of strong shocks or when the flow is going through an expansion, the flow residence time— "time scale associated with the bulk motion of the flow"— can be comparable with the thermal relaxation time. When the flow residence time is comparable to the thermal relaxation time as well as the chemical reaction time— "time scale associated with the chemical reaction rate", the flow will be in thermochemical nonequilibrium. Chemical nonequilibrium is modeled through species conservation equations while thermal nonequilibrium is modeled through internal energies relaxation equations. In high-speed flow conditions involving shockwaves, modeling of nonequilibrium aerothermochemistry becomes extremely important in order to accurately predict the flow parameters of interest like the surface heat flux and stresses.

A typical hyperthermal environment is encountered in atmospheric reentry spacecraft at the Earth's orbit about 40 km and above sea level. The Space Shuttle was flying at the speed of about 7.5 km/s ($M \approx 25$) during its reentry to the Earth's atmosphere. The most popular experimental hypersonic aircraft, X-15 has made multiple hypersonic test flights and has reached up to a maximum speed of about Mach 6.7 [1]. Another experimental aircraft X-43A reached a maximum speed of Mach 9.68 cruising at the altitude of 110,000 ft [2]. At such high velocity, the strong shockwave will initiate thermochemical nonequilibrium in the flow and a proper understanding of this effect becomes paramount to resolving the aerothermal load on a spacecraft. However, modeling thermochemical nonequilibrium has its challenges. Thermodynamic nonequilibrium introduces significant complexity to a reacting high speed aerodynamic flow. Various aspects of flow properties like the chemical reaction rates and transport properties are affected by the thermal nonequilibrium which in turn affects the overall flowfield. Modeling this complex coupling of the thermal nonequilibrium on the flow physics has always been a challenging aspect of hypersonic flows.

During a typical reentry to the Earth's atmosphere, a spacecraft will encounter a variety of flow regimes ranging from free molecular to continuum, transitioning through the



Figure 1.1. Illustration of various high speed flow conditions encountered by different classes of high speed vehicles [3].

rarefied and slip flow regime. Since a significant part of the reentry trajectory falls under the continuum regime, see Fig. 1.1, Computational Fluid Dynamics (CFD) methods —based on Navier-Stokes-Fourier (NSF) laws— become a significant design tool. As mentioned before, the flow complexities adds up due to the presence of shockwaves and thermochemical nonequilibrium effects and its interaction with high speed vehicle. It is probably due to this challenging aspect of high speed flows, most of the popular CFD solvers do not posses the capability of solving thermochemical nonequilibrium flows in a high scalable parallel architecture. Moreover, the design of a high speed vehicle often includes a complex geometry, for example a reentry CubeSat configuration with dragsail. This presents additional challenges to accurately resolve a vehicle's aerothermal characteristics. An illustration of a CubeSat with DragSail is shown in Fig. 1.2.

There are few research codes that have the capability of solving complex nonequilibrium flows, but their access is limited to their developers and collaborators, a few examples being DPLR [4], LAURA [5], US3D [6], LeMANS [7], [8], etc. On the other hand, few open-source nonequilibrium solvers are also available such as COOLFluiD [9] and hy2Foam [10]. With a



Figure 1.2. An illustration of a CubeSat with drag-sail. Source: https://engineering.purdue.edu/CubeSat/missions/ade (visited on Oct-15, 2021).

motivation of developing a nonequilibrium solver that is capable of handing complex geometry and that offers better management of computation resources, the first objective of this work was to develop a nonequilibrium flow solver through implementation of nonequilibrium models to a general purpose equilibrium CFD solver i.e. AN-SYS Fluent. The method of modifying a commercial solver offers an excellent alternative to developing a solver form scratch, as most of the physical and numerical models related to flow modeling are already present in the solver. Shoev et al. in Ref. [11] proposed an implementation of nonequilibrium models in ANSYS Fluent through the use of user-definedfunctions to solve various nonequilibrium flow problems. The work presented here expands on the prior research conducted by Shoev et al. [11]. Development and current capabilities of the nonequilibrium solver, hereby referred to as Fluent-NEQ, are explained in details in Chapter 2 (p. 22).

An important aspect of nonequilibrium flows that demands special attention is the dissociation in thermochemical nonequilibrium. In a typical hypersonic environment, a strong shockwave can excite thermodynamic nonequilibrium in the flow. Besides, the high temperatures behind a shock can have enough thermal energy to dissociate polyatomic/diatomic molecules into their fundamental atomic constituents. Thus, the chemical reactions proceed in thermochemical nonequilibrium conditions. This usually occurs due to a low flow residence time $\tau_{res} = L/V_{\infty}$ — where V_{∞} is the flow speed and L is the length scale of the problem associated with highspeed flows becoming comparable to the thermal energy relaxation time τ_{rlx} as well as the chemical reaction rates τ_{rxn} .

In a system at thermochemical nonequilibrium i.e. $\tau_{res} \approx \tau_{rlx} \approx \tau_{rxn}$, the rate of chemical reactions is greatly affected by the level of nonequilibrium in the system. The chemical reactions proceed in thermodynamic equilibrium if the thermal relaxation time is shorter compared to the chemical reaction time i.e. $\tau_{rlx} < \tau_{rxn}$. Similarly, chemical reactions take place in thermodynamic nonequilibrium if the reaction time scale becomes comparable to the thermal energy relaxation time. In addition, a vibrationally excited molecule requires less thermal collision energy to dissociate compared to a molecule in a low vibrational state. On the other hand, at high temperatures, vibrational energy lost/gain during dissociation the energy lost in dissociation is usually higher than the average vibrational energy of the flow, chemical reactions deplete the vibrational energy faster than it is replenished by the vibrational-translational energy relaxation. It reduces the average vibrational energy of the system that suppresses the dissociation reaction. This complex coupling between vibrational excitation and dissociation is commonly referred to as the vibration-dissociation coupling. The aforementioned vibration-dissociation coupling is one of the most important physics that need to be included while modeling thermochemical nonequilibrium flows.

A general dissociation reaction for a diatomic component of a mixture can be expressed as:

$$AB + M \xrightarrow{k_f} A + B + M$$

where, AB is the diatomic component in a mixture dissociating into monoatomic components A & B, M is the collision partner, and k_f is the kinematic reaction rate. In thermochemical nonequilibrium, the kinematic reaction rates become a function of the translationalrotational temperature $(T_t = T_r = T)$ as well as the vibrational temperature (T_v) i.e. $k_f = k_f(T, T_v)$.

Recent advancement in quantum chemistry has made it possible to calculate reaction rates at nonequilibrium for various collision pairs. Potential Energy Surfaces (PES) ob-

tained through quantum chemistry are used to calculate nonequilibrium reaction rates by Quasiclassical Trajectory (QCT) based methods. The nonequilibrium reaction rates from QCT are obtained considering all possible ro-vibrational states of molecules. QCT calculations for air species have gained growing interest recently and some important reactions have been extensively studied, Ref. [12]–[19]. Furthermore, there has been some attempt to calculate dissociation rates from molecular-based simulations [20]. Although QCT calculations are an excellent way of determining nonequilibrium dissociation reaction rates, the method has its limitations. QCT relies heavily on PES and determining PES for all the reaction pairs in air and calculating reaction rates through QCT can be an extremely (computationally) expensive process. There are also a lot of uncertainties in the PES and QCT methods that are often difficult to quantify, such as the uncertainty in *ab initio* electronic structure, PES fitting error, and QCT statistical errors. In addition, CFD requires macroscopic reaction rates to model chemical reactions which demand some assumption on the distribution of molecules in different vibrational states. Some state-to-state based CFD studies are also common, for example see Ref. [21], but they are particularly limited to binary flow mixture; N_2/N or O_2/O because it involves a large no of conservation equations. For example, under the assumption of harmonic motion, there are 25 vibrational states for an O_2 molecule alone before its vibrational energy becomes greater than the dissociation energy. Despite the recent popularity of QCT calculations, the use of QCT in CFD study of nonequilibrium flow has been somewhat elusive. Hence, empirical and physics-based models are quite popular in CFD in representing nonequilibrium dissociation rates.

One of the most popular vibration-dissociation coupling models in CFD is Park's empirical two-temperature model [22]. Park's two-temperature model introduces a rate-controlling temperature T_{cf} for a dissociation reaction in nonequilibrium. The rate-controlling temperature is taken as an average of the instantaneous translational-rotational temperature (T) and vibrational temperature (T_v) such that $T_{cf} = T^{\alpha_p}T_v^{1-\alpha_p}$, where $\alpha_p = 0.5$ or 0.7. The kinematic reaction rates in Park's model is given in Arrhenius form. The popularity of this model is due to its simplicity rather than its accurate representation of the complex vibration-dissociation coupling. However, Park's two-temperature model does represent some important aspects of vibration-dissociation coupling, such as promoting dissociation when the vibrational excitation is high and suppressing dissociation when the vibrational excitation is low.

There are various physics-based vibration-dissociation coupling models that are available such as Marrone-Treanor [23], Kuznetsov [24], [25], Macheret-Fridman [26], [27], Singh-Schwartzentruber [20], etc. The theoretical/physics-based model derived from some reasonable approximation can provide a more in-depth analysis of vibration-dissociation coupling. Besides, the models do not require the availability of *ab initio* QCT or PES data. Recently, the physics-based models have received a growing interest in both CFD and Direct Simulation Monte Carlo (DSMC) community, see Ref. [11], [20], [28]–[30].¹ The classical impulsive dissociation model by Macheret et al. [26], [27], [31] was recently revisited by Luo et al. in Ref. [29] and has shown promising results. The classical impulsive model known as the Macheret-Fridman (MF) model since then has been extended to DSMC referring it to as the MF-DSMC model in Ref. [32], [33]. The previous formulation of the MF model, applicable to CFD, only considered homonuclear diatomic molecules [26], [27], [29] like $N_2 \& O_2$, so its application was limited to binary gas mixture; N_2 / N or O_2 / O . With a motivation of overcoming this limitation, the next objective of this work was to develop a general form of classical impulsive dissociation model, hereby referred to as MF-CFD model. The development of MF-CFD model involves revisiting the classical impulsive dissociation theory for a heteronuclear diatomic molecule. The developed MF-CFD model facilitates the study of nonequilibrium air with heteronuclear species like nitric oxide (NO) as one of its mixture components. The details regarding the development of MF-CFD model and its capabilities of solving various nonequilibrium flow are given in Chapter 3 (p. 46).

The nonequilibrium solver development as a part of this work provides a unique capability to investigate reentry aerothermodynamics of spacecrafts with complex geometry. An example of such a complex reentry spacecraft is CubeSat with drag enhancing devices. An experimental deorbiting CubeSat configuration that uses dragsail for effective disposal of CubeSat post-mission is in active development by researchers at Purdue University. The experimental CubeSat is known as the Aerodynamic Deorbit Experiment (ADE) CubeSat [34],

¹↑Although both NSF based methods and DSMC methods are computational modeling of fluid/gas dynamics, the NSF based methods are commonly referred to as the Computational Fluid Dynamics (CFD).

[35], Fig. 1.2. The study represents a valuable effort in mitigating the space debris from the most treasured low earth orbits. As the world moves towards sustainability, research of such type will contribute significantly towards maintaining the availability of precious low earth orbits.

An accurate prediction of reentry trajectory of a CubeSat is important to reduce threats to air traffic as well as ground habitat. The DSMC methods are often used to access the aerothermodynamics of the reentry CubeSat, however the methods become computationally expensive as the flow reaches near-continuum regime. With a motivation of complementing the DSMC methods in predicting the reentry trajectory, especially at altitudes in the near-continuum regime, **the next objective of this work was to investigate aerothermodynamics of a reentry CubeSat with dragsail at altitudes corresponding to near-continuum regime.** An assessment of the flow prediction capabilities of the CFD methods at high altitudes, with respect to resolving the aerothermal load on a reentry Cube-Sat with dragsail, is given in Chapter 4 (p. 83).

1.1 Research Objectives

The primary research objectives and its specific objectives are listed below:

- 1. Fluent-NEQ Development
 - (a) Develop a solver through implementation of nonequilibrium models in ANSYS Fluent package
 - (b) Verify the Fluent-NEQ solver through benchmark cases
- 2. MF-CFD Development
 - (a) Re-derive Macheret-Fridman classical impulsive model for dissociation of a general heteronuclear molecule
 - (b) Investigate various nonequilibrium flows with the MF-CFD model implemented to Fluent-NEQ solver
- 3. Reentry Aerothermodynamics of CubeSat with Dragsail

- (a) Resolve aerothermal load on a CubeSat with dragsail in near-continuum regime
- (b) Assess flow prediction capabilities of CFD based methods at high altitudes

Each objectives are visited in details in the subsequent chapters.

2. FLUENT-NEQ DEVELOPMENT

Fluent-NEQ is a nonequilibrium add-on solver developed through implementation of nonequilibrium models in air to the ANSYS Fluent solver. The nonequilibrium models are introduced to the Fluent solver using the user-defined-functions (UDFs). The work presented here expands on the prior research conducted by Shoev et al. [11]. The nonequilibrium solver developed through modifications of ANSYS Fluent in Ref. [11] was able to successfully model various nonequilibrium flow problems and it has been continuously used as a research tool for investigating different aspects of nonequilibrium flow, see Ref. [28], [36]–[39]. This work presents similar development of a nonequilibrium CFD solver with added improvements and capabilities. The development of Fluent-NEQ further highlights the effectiveness of this approach of modifying a commercial solver to investigate practical high speed nonequilibrium flow problems.

Various aspects of nonequilibrium flow modeling in Fluent-NEQ are given as follows:

2.1 Thermodynamic Nonequilibrium

For nonequilibrium flows, the internal energies of a polyatomic species can not be represented by a single temperature. Different modes of internal energy should be represented by different modes of temperature i.e. translational mode of energy with translational temperature (T_t) , rotational mode of energy with rotational temperature (T_r) , vibrational mode of energy with vibrational temperature (T_v) , and electronic mode of energy with electronic temperature (T_e) . Monoatomic molecules only have translational and electronic energies while polyatomic molecules can have all four modes of energy. However, the characteristic temperatures related to the electronic mode of energy are usually very high. The electronic excitation can be ignored for low to moderate Mach number flows and it only becomes important to include electronic excitation for flows with extremely high Mach number, $M \geq 15$ in air [40]. Thus for most engineering applications, expressing internal energies in terms of translational, rotational, and vibrational modes is sufficient.

Even in the presence of a strong shockwave, the rotational energy reaches equilibrium within a few mean-free-path distance and requires very few collisions to reach equilibrium while the vibrational energy has comparably longer relaxation. A study in Ref. [41] has demonstrated the faster rotational relaxation in a Nitrogen flow even at extremely high Mach number, $M_{\infty} = 10$, using Direct Simulation Monte Carlo (DSMC) methods. Since the rotational energy relaxation are very fast compared to vibrational energy relaxation, the translational and rotational modes of energy can be assumed to be in thermal equilibrium for most aerodynamic flows and can be represented by a single translational-rotational temperature (T_{tr}). Also, under the assumption that the Vibrational-Vibrational (V-V) relaxation occurs very fast (equilibrium among different vibrational excitation states), the thermodynamic nonequilibrium can be successfully modeled using two-temperature approach, T_{tr} and T_v . For convenience, T_{tr} will simply be represented by T from hereafter.

In this study, the thermal nonequilibrium is modeled through two internal energy relaxation equations- translational-rotational (E_{tr}) energy relaxation and vibrational (E_v) energy relaxation. The internal energy relaxation equations have vibrational-translational (VT) relaxation terms that represent the energy transfer between translational-rotational and vibrational modes of energy.

2.2 Governing Equations

Governing equations for a chemically reacting nonequilibrium flow in a compact form are as below:

$$\partial_t U + \nabla \cdot \vec{F^c} - \nabla \cdot \vec{F^\nu} = W \quad \text{in } \Omega, \, t > 0 \tag{2.1}$$

$$U = \begin{bmatrix} \rho \\ \rho_{s} \\ \rho u_{1} \\ \rho u_{2} \\ \rho u_{3} \\ \rho E_{tr} \\ [\rho_{k}e_{v,k}] \end{bmatrix}, \vec{F_{i}^{c}} = \begin{bmatrix} \rho u_{i} \\ \rho_{s} u_{i} \\ \rho u_{i} u_{1} + P \delta_{i1} \\ \rho u_{i} u_{2} + P \delta_{i2} \\ \rho u_{i} u_{3} + P \delta_{i3} \\ (\rho E_{tr} + P) u_{i} \\ [\rho_{k}e_{v,k} u_{i}] \end{bmatrix}, \vec{F_{i}^{\nu}} = \begin{bmatrix} 0 \\ -J_{s,i} \\ \tau_{i1} \\ \tau_{i2} \\ \tau_{i3} \\ q_{tr,i} + u_{j}\tau_{ij} - h_{s}J_{s,i} \\ [q_{vk,i} - e_{v,k}J_{k,i}] \end{bmatrix}, W = \begin{bmatrix} 0 \\ w_{s} \\ 0 \\ 0 \\ -h_{s}^{0}w_{s} - S_{v} \\ [S_{v,k}] \end{bmatrix}$$
(2.2)

$$P = \sum_{s=1}^{N_s} P_s = \sum_{s=1}^{N_s} (\rho_s R_u / M_{w,s} T) = \rho T R_u \sum_{s=1}^{N_s} (Y_s / M_{w,s})$$
(2.3)

$$\rho_{N_s} = \rho - \sum_{s=1}^{N_s - 1} \rho_s \quad \text{Or} \quad Y_{N_s} = 1 - \sum_{s=1}^{N_s - 1} Y_s$$
(2.4)

where,

$$E_{tr} = u_{i}u_{i}/2 - P/\rho + Y_{s}h_{s}$$

$$h_{s} = \int_{T_{ref}}^{T} (C_{p,s})_{tr} dT$$

$$(C_{p,s})_{tr} = \frac{1}{2} \frac{R_{u}}{M_{w,s}} (f_{tr,s} + 2)$$

$$\tau_{ij} = \mu(\partial_{j}u_{i} + \partial_{i}u_{j} - \frac{2}{3}\delta_{ij}\nabla \cdot \vec{u})$$

$$(2.5)$$

 $J_{s,{\rm i}}=-\rho D_s\partial_{\rm i}Y_s \quad ({\rm no \ summation \ on \ s})$

$$q_{tr,i} = \eta_{tr} \partial_i T$$

$$q_{vk,i} = \eta_{v,k} \partial_i \mathbf{e}_{v,k}, \quad \eta_{v,k} = Y_k \mu_k \quad \text{(no summation on k)}$$

$$S_{v,k} = \dot{\mathbf{e}}_{v,k}^{VT} + \dot{\mathbf{e}}_{v,k}^{react}$$
 and $S_v = \sum_{k=1} S_{v,k}$

Here N_s is the total number of species in the mixture, ρu_1 , ρu_2 , ρu_3 are the flux component of x-momentum, y-momentum and z-momentum respectively, ρE_{tr} is the flux of translational-rotational energy, and $\rho_k e_{v,k}$ is the flux of average vibrational energy of k^{th} species out of N_m total number of molecular/polyatomic species in the mixture. The vibrational relaxation equation for each molecular/polyatomic species in the mixture is solved separately. Thus, the block $\left[\cdot\right]_{N_m}$ in Eq. (2.2) represents a total of N_m number of vibrational relaxation equations. $(C_{p,s})_{tr}$ is the specific heat at constant pressure related to translational and rotational degrees of freedom of the s^{th} component of the mixture, $f_{tr,s}$ is the number of translational and rotational degrees of freedom of a species, τ_{ij} is the viscous stress with the *Stoke's hypothesis* for second viscosity term, $J_{s,i}$ is the term representing the mass flux due to diffusion determined using the *Fick's law*, D_s is the effective diffusion coefficient for a species-s, μ is the dynamic viscosity of the mixture, η_{tr} is the translational rotational thermal conductivity coefficient, $\eta_{v,k}$ is the conductivity of vibrational energy for a polyatomic species k derived using an *Eucken relation* [42], [43] and S_v is the source term that represents the transfer of energy between translational-rotational and vibrational mode as well as the relationship between vibrational relaxation and chemical reactions.

For most practical problems involving diatomic molecules, the simple harmonic oscillator model, Eq. (2.6), proved to be a reasonable assumption for representing average vibrational energy. The average vibrational energy for a diatomic species is given as:

$$e_{v,s}(T_v) = \frac{\Theta_{v,s} R_u / M_{w,s}}{\exp(\Theta_{v,s} / T_v) - 1} \qquad s = \text{molecule}$$
(2.6)

$$(C_{v,s})_{vib} = \frac{\partial \mathbf{e}_{v,s}}{\partial T_v} = \frac{R_u}{M_{w,s}} \left(\frac{\Theta_{v,s}}{T_v}\right)^2 \frac{\exp(\Theta_{v,s}/T_v)}{[\exp(\Theta_{v,s}/T_v) - 1]^2}$$
(2.7)

Here, Θ_v is the characteristic vibrational temperature of a diatomic molecule and $(C_{v,s})_{vib}$ is the specific heat at a constant volume related to vibrational degrees of freedom of the s^{th} species. Various physio-chemical properties of different species considered in this study are given in Table B.1.

2.3 Transport Models

The transport properties of a fluid such as laminar viscosity, thermal conductivity, and diffusion coefficients are usually calculated using the kinetic theory of gases for high temperature flows. The dynamic viscosity of an individual species in a mixture by the *Hirschfelder* model [44] is given as:

$$\mu_s = 2.6693 \times 10^{-6} \times \frac{\pi \sqrt{M_{w,s}T}}{\pi \bar{\Omega}_{ss}^{(2,2)}}$$
(2.8)

The collision cross-sections $\pi \bar{\Omega}_{sr}^{(l,s)}$ given here are same as $\pi \sigma_{sr}^2 \bar{\Omega}_{sr}^{(l,s)*}$, that is often referred in the literature. The collision cross-sections can be obtained either through the *Lennard-Jones (LJ)* parameters or through a curve fit of available data. This work utilizes the collision cross-sections given by Gupta et al. [45]. The curve fit data for the collision cross-sections by Gupta et al. is given in Table B.2 and the collision cross-sections from Table B.2 can be computed as:

$$\pi \bar{\Omega}_{sr}^{(l,l)} = D_{(l,l)} T^{\left[\left(A_{(l,l)} ln(T) + B_{(l,l)} \right) ln(T) + C_{(l,l)} \right]}$$
(2.9)

The translational-rotational component of the thermal conductivity using *Eucken correction* [44] is given as:

$$\eta_{tr,s} = \frac{15}{4} \times \frac{R_u}{M_{w,s}} \mu_s \left[\frac{4}{15} \times \frac{(C_{p,s})_{tr} M_{w,s}}{R_u} + \frac{1}{3} \right]$$
(2.10)

The most common mixing law to compute gas mixture dynamic viscosity (μ) and thermal conductivity (η) is the Wilke's semi-empirical mixing formula [46]. However, the Wilke's ideal gas mixing law lacks acceptable accuracy at high temperatures and the study in Ref. [47] has shown the Wilke's law to be computationally expensive compared to more accurate high temperature Gupta-Yos mixing law [45]. This work utilizes the Gupta-Yos mixing law to calculate transport properties of a gas mixture. The Gupta-Yos mixing law is:

$$\mu = \sum_{s} \left[\frac{x_s M_{w,s} / N_A}{\sum_r x_r \Delta_{sr}^{(2)}(T)} \right]$$
(2.11)

$$\eta_{tr} = \frac{15}{4} k_b \sum_{s} \frac{x_s}{\sum_r \alpha_{sr} x_r \Delta_{sr}^{(2)}(T)} + k_b \sum_{s \neq atoms} \frac{x_s}{\sum_r x_r \Delta_{sr}^{(1)}(T)}$$
(2.12)

$$\eta_v = k_b \sum_{s \neq atoms} \frac{x_s(C_{v,s})_{vib} M_{w,s}/R_u}{\sum_r x_r \Delta_{sr}^{(1)}(T)}$$
(2.13)

where, x_s is the species mole fraction, η_v is the vibrational thermal conductivity and the collision terms: $\Delta_{sr}^{(1)} \& \Delta_{sr}^{(2)}$ and α_{sr} are:

$$\Delta_{sr}^{(2)} = \frac{16}{5} \left[\frac{2M_{w,s}M_{w,r}}{\pi R_u T(M_{w,s} + M_{w,r})} \right]^{1/2} \pi \bar{\Omega}_{sr}^{(2,2)} \times 10^{-20}$$
(2.14)

$$\Delta_{sr}^{(1)} = \frac{8}{3} \left[\frac{2M_{w,s}M_{w,r}}{\pi R_u T(M_{w,s} + M_{w,r})} \right]^{1/2} \pi \bar{\Omega}_{sr}^{(1,1)} \times 10^{-20}$$
(2.15)

$$\alpha_{sr} = 1 + \frac{\left(1 - M_{w,s}/M_{w,r}\right) \left[0.45 - 2.54(M_{w,s}/M_{w,r})\right]}{\left[1 + M_{w,s}/M_{w,r}\right]^2}$$
(2.16)

The effective diffusion coefficient, D_s of a species in a mixture is given by:

$$D_s = \frac{(1 - x_s)}{\sum_{r \neq s} (x_r / D_{sr})}$$
(2.17)

where D_{sr} is the binary diffusion coefficient. The binary diffusion coefficient can be computed as:

$$D_{sr} = \frac{k_b T}{P \Delta_{sr}^{(1)}(T)}$$
(2.18)

2.4 Vibrational-Translational (VT) Energy Relaxation

Assuming Boltzmann distribution (equilibrium) for molecules at different vibrational states- assuming that the V-V relaxation occurs very fast, the expression for the rate of change of vibrational energy of a gas through collisions is given by the famous *Landau-Teller* formula [48]:

$$\dot{\mathbf{e}}_{v,s}^{VT} = \frac{\rho Y_s \left(\mathbf{e}_{v,s}(T) - \mathbf{e}_{v,s}(T_v) \right)}{\tau_{v,s}}$$
(2.19)

Here, $\tau_{v,s}$ is the species vibrational relaxation time. Equation (2.19) also represents the instantaneous rate at which vibrational energy is approaching the equilibrium. The Landau-Teller formula is only valid for diatomic molecules that are harmonic oscillator as it only considers a single quantum jump between different energy levels. Quantum jumps between

multiple energy levels can occur for anharmonic molecules but the probability of such jump is mostly small.

The relaxation time of a species, $\tau_{v,s}$ is usually taken as an average between different collision pairs. The Landau-Teller relaxation time between a collision pair, τ_{sr} is commonly determined from the *Millikan-White correlation* [49]. The relaxation time utilizing the Millikan-White correlation is given as:

$$\langle \tau_{MW,s} \rangle = \frac{\sum_{r} x_{r}}{\sum_{r} (x_{r}/\tau_{sr})}$$
(2.20)

$$P\tau_{sr} = \exp\left[A_{sr}(T^{-1/3} - B_{s,r}) - 18.42\right] \quad (atm \cdot sec), \tag{2.21}$$

$$A_{sr} = 1.16 \times 10^{-3} m_{sr}^{1/2} \Theta_{v,s}^{4/3}, \quad B_{s,r} = 0.015 m_{sr}^{1/4}, \quad m_{sr} = \frac{M_{w,s} \times M_{w,r}}{M_{w,s} + M_{w,r}}$$

The Millikan-White correlation was obtained using a limited number of collision pairs and does not accurately predict the relaxation time for collision pairs like N₂ + O, O₂ + O, and NO + NO in air. Park suggested modifications to Millikan-White parameters A_{sr} and B_{sr} for some collision pairs so that they properly represent experimental observation while retaining the temperature dependency for the relaxation time [50]. The modified Millikan-White parameters from Ref. [50] is given in Table B.3.

For temperatures above 8,000 K, Park found that the Millikan-White correlation for the relaxation time overpredicts the effective cross-sections and suggested a correction in Ref. [22]. Park's correction, $\tau_{c,s}$ to the relaxation time, that is also known as the collision limited relaxation time, is given as:

$$\tau_{c,s} = \frac{1}{\sigma_s C_s n_s} \tag{2.22}$$

$$\sigma_s = 10^{-20} \left(\frac{50,000}{T}\right)^2 \quad (m^2) \tag{2.23}$$

$$C_s = \sqrt{\frac{8R_u T}{\pi M_{w,s}}} \quad (m/s) \tag{2.24}$$

$$n_s = \frac{N_A \rho Y_s}{M_{w,s}} \quad (\#/m^3)$$
 (2.25)

where σ_s is the limiting cross section, C_s is the average molecular velocity of the species s, and n_s is the species number density. Thus the relaxation time for a species in Eq. (2.19) with Park's high temperature correction becomes:

$$\tau_{v,s} = \langle \tau_{MW,s} \rangle + \tau_{c,s} \tag{2.26}$$

2.5 Chemical Reactions in Vibrational Nonequilibrium

The chemical reactions in this work are modeled through the finite rate chemistry. A chemical reaction in a generic form can be represented as:

$$\sum_{s}^{N_{s}} \nu_{s,\gamma}' X_{s} \stackrel{k_{f,\gamma}}{\overleftarrow{k_{b,\gamma}}} \sum_{s}^{N_{s}} \nu_{s,\gamma}'' X_{s}$$

$$(2.27)$$

Here, X_s denotes a chemical species and $\nu''_{s,\gamma}$ and $\nu'_{s,\gamma}$ are the stoichiometric coefficients of the products and reactants in a reaction γ , respectively, $k_{b,\gamma}$ and $k_{f,\gamma}$ are the kinematic reaction rates for the forward and backward reactions, respectively. The rate of gain/loss of a chemical species s in a reaction γ is:

$$w_{s,\gamma} = (\nu_{s,\gamma}'' - \nu_{s,\gamma}') \left(k_{f,\gamma} \prod_{j}^{N_s} \left(\frac{\rho_j}{M_{w,j}} \right)^{\nu_{j,\gamma}'} - k_{b,\gamma} \prod_{j}^{N_s} \left(\frac{\rho_j}{M_{w,j}} \right)^{\nu_{j,\gamma}''} \right)$$
(2.28)

The source term in a species transport equation representing the rate of gain/loss of a chemical species due to chemical reactions is obtained as:

$$w_s = M_{w,s} \sum_{\gamma}^{N_{rxn}} w_{s,\gamma} \quad \text{(no summation on s)}$$
(2.29)

The kinematic reaction rates for chemical reactions are usually obtained through experiments and are only available for reacting species that are in thermodynamic equilibrium. But, the molecules at higher states of vibrational energy dissociate easily and require less energy during a collision to dissociate. The kinematic reaction rates are thus affected by the vibrational excitation and it requires multi-temperature model to accurately represent the kinematic reaction rates in thermodynamic nonequilibrium. The precise accounting for this vibration-dissociation coupling is however extremely complex. A more detail account of this phenomena is given in Chapter 3 (p. 46). One of the most popular and simple model to take account of the vibration-dissociation coupling was developed by Park [22]. The two-temperature Park's model introduces an average temperature between instantaneous translational-rotational and vibrational temperatures i.e. $T^{\alpha}T_{v}^{1-\alpha}$ with $\alpha = 0.5$ or 0.7 as the rate controlling temperature for dissociation reactions. The difference in the convective heating rate for different α in Park's model has been found to be very small, see Ref. [51].

The implementation of nonequilibrium chemistry is paramount to resolving aerothermal load on a high speed vehicle. A double cone configuration with nonequilibrium, equilibrium, and frozen chemistry was investigated in Ref. [52] for a variety of flow conditions. The study has highlighted the importance of proper thermochemistry modeling in estimating thermal load, especially in high enthalpy conditions through comparison with experiments.

The kinematic reaction rates for the forward reaction in Eq. (2.27) with Park's rate controlling temperature in an Arrhenius form is:

$$k_{f,\gamma}(T_{cf}) = AT_{cf}^{\ b} \exp\left(\frac{-E_d/R_u}{T_{cf}}\right)$$
(2.30)

where, constants A, b and E_d in the kinematic reaction rates for various reactions considered in this study are taken from Park 1990/1993 [22], [50] reaction sets and the reaction constants are included in Table B.4 with their respective forward reaction rate controlling temperature T_{cf} .

In this study, the backward reaction rates are determined from equilibrium constant K_{eq} in the following way:

$$k_{b,\gamma}(T_{cb}) = \frac{k_{f,\gamma}(T_{cb})}{K_{eq,\gamma}(T_{cb})}$$

$$(2.31)$$

The equilibrium constants are obtained from Park 1990 [22] through the curve fit of partition functions at equilibrium. The backward reaction rate controlling temperature (T_{cb}) for different reactions are also present in Table B.4. The source term for a vibrational energy relaxation equation that represents the change in vibrational energy due to chemical reactions, Eq. (2.5), in Park model is given as:

$$\dot{\mathbf{e}}_{v,s}^{react} = \mathbf{e}_{v,s} w_s \quad \text{(no summation on s)}$$
 (2.32)

The form presented here represents the non-preferential vibration-dissociation coupling. It means the loss/gain of polyatomic components in a chemical reaction does not change the average vibrational energy. The polyatomic components are assumed to take away the average vibrational energy during the dissociation and are assumed to be generated with the average vibrational excitation through recombination reactions. In reality, the dissociating molecules take away the vibrational energy that is some fraction of the dissociation energy, which is usually much higher than the average vibrational energy. Similarly, the polyatomic molecules that are generated in recombination reactions are at higher vibrational excitation than the average vibrational energy. However, the Park's model does not provide an expression for the mean energy removed in dissociation. A detailed insight into the energy removed in a dissociation reaction is given in Chapter 3 (p. 46).

2.6 Modifications to Fluent

ANSYS Fluent allows the solution of an additional scalar transport equation through User Defined Functions $(UDFs)^1$. A general form of the scalar transport equation in Fluent is represented as:

$$\frac{\partial}{\partial t}(\rho\Phi_k) + \nabla \cdot (\rho\vec{u}\Phi_k - \Gamma_k\nabla\Phi_k) = S_{\Phi_k}$$
(2.33)

The vibrational relaxation equation for a polyatomic/molecular species in the similar form will be:

$$\frac{\partial}{\partial t}(\rho_s \mathbf{e}_{v,s}) + \nabla \cdot \left((\rho_s \vec{u} + \vec{J}_s) \mathbf{e}_{v,s} - \eta_{v,s} \nabla \mathbf{e}_{v,s} \right) = S_{v,s}$$
(2.34)

Here, we have $\Phi_k = e_{v,s}$. The flux component in Eq. (2.34) is different from the default flux component in Eq. (2.33), so UDF: DEFINE_UDS_FLUX was utilized to introduce the flux component of the vibrational relaxation equation to the solver. Similarly, other components

 $^{^1 \}uparrow \rm Refer$ to ANSYS Fluent UDF Manual for more detail

of the vibrational relaxation equation such as transient, diffusion, and source terms are also introduced in the solver through their respective UDFs; UDF: DEFINE_UDS_UNSTEADY, UDF: DEFINE_DIFFUSIVITY, and UDF: DEFINE_SOURCE. Here, the average vibrational energy ($e_{v,s}$) for each polyatomic species is solved through the scalar transport equation and the vibrational temperature (T_v) is determined from calculated $e_{v,s}s$, using the UDF: DEFINE_ADJUST. The conservation equations for vibrational energy introduced in the solver are solved in a decoupled manner. The governing equations for the bulk flow— with translational-rotational energy— are first solved simultaneously and then the vibrational energy relaxation is solved using the computed flow properties. The vibrational components of the flow are then used to solve the bulk flow during the next iteration. This method of solving additional equations in a decoupled manner is also common while simulating turbulent flows in RANS modeling where the turbulence equations are solved similarly.

ANSYS Fluent in its core is an equilibrium solver and the components of the flow solution that is affected by the nonequilibrium effects had to be modified as well. Thus, the kinematic reaction rates (UDF: DEFINE_VR_RATE), transport properties (UDF: DEFINE_PROP-ERTY), boundary conditions (UDF: DEFINE_PROFILE), and solution initialization (UDF: DEFINE_INIT) were also modified in the solver using their respective UDFs. The developed nonequilibrium solver is capable of solving transient and steady state nonequilibrium flow problems in both two and three dimensions.

2.7 Verification of Fluent-NEQ

The current implementation of nonequilibrium models in Fluent-NEQ were successfully used to solve various high speed nonequilibrium flow problems. The flow solutions were obtained with an implicit compressible steady state solver (density based solver). The convective fluxes were computed using AUSM+ flux vectoring with second order upwind scheme and the viscous flow gradients were computed utilizing the Green-Gauss node-based method. The cases were run on a typical Intel Xeon workstation running at 2.5 GHz with 126 GBmemory and 40 cores with ANSYS Fluent v19.4.0.

2.7.1 Nonequilibrium hypersonic flow over a cylinder

A partially dissociating Nitrogen flow over various cylinders was experimentally studied by Hornung in 1972 [53]. These experiments are often used as a nonequilibrium CFD code verification case [54], [55]. Hornung has presented interferograms of flowfield (fringe patterns) around the cylinders of various sizes from his experiments. The computed flowfield through Fluent-NEQ were compared with the experiment using the relation of change in density ($\Delta \rho$) to the fringe patterns given by Hornung [53] as:

$$\Delta \rho = \frac{4160F\lambda}{l(1+0.28Y_N)}, \quad \rho \text{ in } kg/m^3$$
(2.35)

where, F is the fringe number, λ is the wavelength, and l is the experiment's geometrical path.

In this study, a non-diffusive flow over a cylinder of 2 in diameter was considered, similar to that in Ref. [54]. The freestream conditions for this case are given in Table 2.1. The low Knudsen number, $\text{Kn} = 7.13 \times 10^{-4}$, suggests the flow is in continuum regime.

Table 2.1. Freestream conditions for hypersonic cylinder with 2 in diameter.

V_{∞}	$5590 \mathrm{~m/s}$
T_{∞}	1833 K (= $T_{v,\infty}$)
P_{∞}	2910 Pa
M_{∞}	6.14
Y_N	0.073
Y_{N_2}	0.927
Kn	7.13E-4
$h_0 - h_{298K}$	$17.44 \mathrm{~MJ/kg}$

The flowfield in Fluent-NEQ matches well with the experiment for the most part of the flow. There are slight differences along the stagnation line between the experiment and Fluent-NEQ result, evident in Fig. 2.1a. The evolution of the bow shockwave is similar to in the experiment. The shockwave standoff distance is well within 0.3% of the experiment, Fig. 2.1b. The slight differences in the flowfield compared to the experiment can be attributed to the lack of information regarding the nonequilibrium state at the freestream. Also, Park's



Figure 2.1. Comparison of (a) flowfield (fringe patterns; $\lambda = 5330$ Å, l = 6 in) and (b) shock standoff distance with experiments [53] in a hypersonic cylinder with 2 in diameter.

two-temperature model is known to produce results closer to the equilibrium state. In overall, the results match fairly well with the experiment and it indicates proper implementation of the nonequilibrium models and boundary conditions in Fluent-NEQ.

2.7.2 Mars entry spacecraft

The Martian entry spacecraft model was experimentally studied by Hollis [56] in which the surface heat flux across the spacecraft model was measured. This model was later investigated computationally by Hollis and Perkins [57]. The Mars entry spacecraft model has 70° blunted conical forebody with a nose radius (R_n) of 12.7 mm and a base radius (R_b) of 25.4 mm. It has a 40° afterbody conical section with a 1.27 mm corner radius (R_c) between the forebody and afterbody section. The schematic diagram for the model is shown in Fig. 2.2 with key geometrical features used in this study. In this study, only the forebody of the model was investigated as an axisymmetric flow problem with 5 species reacting air mixture; N₂, O₂, NO, N, and O. The freestream conditions for this case are presented in Table 2.2. The no-slip thermal boundary condition was specified at the wall with zero-diffusion flux for the species (non-catalytic wall). The mesh generated for this model consists of quadrilateral elements only. Regarding the computational cost, the most refined grid took about 6 hrs of computation time with 10 grid partitions.



Figure 2.2. Schematic diagram of Mars entry spacecraft model.

V_{∞}	$5162 { m m/s}$
T_{∞}	1113 K (= $T_{v,\infty}$)
$ ho_{\infty}$	$5.71\text{E-}3 \text{ kg/m}^3$
M_{∞}	7.9
T_w	300 K
Y_{N_2}	0.767
Y_{O_2}	0.233
Kn	2.8E-4
$h_0 - h_{298K}$	$14.20 \mathrm{~MJ/kg}$

 Table 2.2.
 Freestream conditions for Mars entry spacecraft model.

For a grid convergence study, three different sets of grids were created with grid size for the first cell normal to the wall boundary (Δs) as 1E-7, 1E-6, and 1E-5 m. The heat flux across the forebody of the spacecraft was used as a parameter to test for grid convergence. The heat flux through the wall in Fluent-NEQ was calculated using the contribution from both translational-rotational and vibrational modes of energy i.e. $q_w = -\eta_{tr} \nabla_n T - \eta_v \nabla_n T_v$. Figure 2.3a shows the heat flux across the model of Mars entry spacecraft for different grid sizes with S being the distance measured along the body starting from the flow stagnation



Figure 2.3. (a) Effect of grid resolution on heat flux across the forebody and (b) temperatures along the stagnation line in Martian entry spacecraft model.

region. The grid convergence study reveals that the heat flux is sensitive to the grid size mostly towards the stagnation region only. The heat flux does not change with grid size for the most part of the forebody $(S/R_b \ge 0.2)$. The maximum heat flux- at the stagnation region- only changes by ~ 5% when the grid size is decreased from $\Delta s = 1$ E-6 m to $\Delta s =$ 1E-7 m. Hence, the flow solution with a grid size of $\Delta s = 1$ E-7 m is considered to be a grid independent solution. Additionally, one can see that the heat flux near the stagnation region shows some oscillatory behavior. This behavior is mostly numerical and can be attributed to the inviscid flux calculation method. The oscillation is however damped with the decrease in grid size, evident in Fig. 2.3a. Despite the oscillation, the mean across the oscillation— with grid size $\Delta s = 1$ E-7 m— shows almost asymptotic heat flux towards the stagnation region which is expected for a blunt body like Mars entry spacecraft. The grid refinement only affects the peak translational-rotational and vibrational temperatures. The temperatures elsewhere are mostly independent of the grid resolution, Fig. 2.3b.

The heat flux across the forebody of the model predicted by Fluent-NEQ is within an acceptable range of experimental uncertainty, Fig. 2.4a. Here, the plot also shows various results present in the literature [8], [57] and the heat flux obtained with Fluent-NEQ is found
to be consistent with other published work. The slight discrepancies in these results could be due to the differences in the numerical schemes and some thermodynamic models used across the studies. The study in Ref. [8], [57] used the *modified Steger-Warming* flux-vector splitting method for computing inviscid fluxes whereas Fluent-NEQ used AUSM+. In terms of differences in the thermodynamic models, the results in Ref. [57] were obtained using the semi-empirical *Wilke's ideal gas mixing law* [43] whereas in Ref. [8], the results were obtained utilizing the high temperature *Gupta-Yos mixing law* same as in Fluent-NEQ.



Figure 2.4. (a) Comparison of surface heat flux with experiment [56] and published results [8], [57] and (b) variation of temperatures along the stagnation line in Martian entry spacecraft model.

Evident in Fig. 2.4b, the maximum translational-rotational temperature behind the shockwave is around 12,000 K while the maximum vibrational temperature is around 7,200 K. Here, the temperature variation along the stagnation line are compared with the result in Ref. [58]. The shock standoff distance and the maximum translational-rotational temperature in Fluent-NEQ are comparable with the results in Ref. [58]. The maximum vibrational temperature in Fluent-NEQ is slightly lower than in Ref. [58]. The variation of mass fractions of the chemical species along the stagnation line in Fig. 2.5a shows the decrease in mass fractions of N₂ and O₂ behind the shockwave due to dissociation reactions. The mass

fractions of O and N near the boundary decrease drastically due to recombination near the cold wall ($T_w = 300$ K). The concentration of Nitric oxide (NO) is higher right behind the shockwave, Fig. 2.5b. Generation of atomic Oxygen (O) due to the dissociation of O₂ facilitates the formation of NO behind the shockwave through the exchange reactions between N₂ and O. The mass fractions variation along the stagnation line shows excellent agreement with the results in Ref. [58]. The variation of axial flow velocity across the body of the spacecraft is shown in Fig. 2.6.



Figure 2.5. (a) Mass fractions of chemical species along the stagnation line and (b) NO mass fraction contour over the Martian entry spacecraft model.

2.8 Importance of Nonequilibrium Modeling: Fluent-NEQ vs. Fluent-1T

This section investigates the importance of vibrational energy relaxation modeling for high speed nonequilibrium flows by a comparison between nonequilibrium and equilibrium flow solutions. In one-temperature (1T) (equilibrium) modeling, the total energy conservation equation is solved instead of the translational-rotational and vibrational relaxation equations. The energy conservation equation includes the vibrational contribution to the specific heat capacity as well as the thermal conductivity but these properties are a function



Figure 2.6. Axial velocity contour over the Martian entry spacecraft model.

of a single temperature $(T_t = T_r = T_v)$ that represents the translational, rotational, and vibrational modes of energy in equilibrium. Since there is no energy relaxation (or the internal energy relaxation happens extremely fast) in equilibrium, no additional source terms are present in the energy conservation equation.

For a consistent comparison with the Fluent-NEQ solution, the C_p for a diatomic species are specified as $C_p = (C_p)_{tr} + (C_p)_{vib}$ in 1T modeling, where $(C_p)_{vib}(T)$ was calculated using the Simple Harmonic Oscillator assumptions, Eq. (2.6). Moreover, the Gupta-Yos high temperature mixing laws were used in the 1T modeling similar to the Fluent-NEQ.

The surface heat flux and the temperatures along the stagnation line in the Martian entry spacecraft model are shown in Fig. 2.7a and 2.7b, respectively. Surface heat flux prediction in 1T equilibrium solution is higher compared to the 2T Fluent-NEQ solution. The temperatures variation along the stagnation line shows that the shock standoff distance is slightly lower in the 1T solution compared to Fluent-NEQ. A better agreement of 2T surface heat flux predictions with the experimental measurements compared to equilibrium heat flux indicates that the Martian entry spacecraft model is a good nonequilibrium CFD



Figure 2.7. (a) Comparison of surface heat flux and (b) temperatures variation along the stagnation line between Fluent-NEQ and Fluent-1T equilibrium solutions in Martian entry spacecraft model.

verification case. In addition, the results show that it is important to model the internal energy relaxation in high speed nonequilibrium flows for a better surface heat flux prediction.

2.9 Slip Models for Near-Continuum Flows

The Navier-Stokes-Fourier (NSF) hydrodynamic equations assume no-slip gas-surface interaction and linear relationship between stress and strain. Degree of flow rarefaction is often characterized based on the non-dimensional Knudsen number (Kn) which is given as:

$$Kn = \frac{\lambda}{L_c},\tag{2.36}$$

where, λ is the mean-free-path of the molecules and L_c is a characteristic length. The continuum regime is equivalent to Kn < 0.01. For a flow with a higher Knudsen number, the first order approximation of the stress tensor and other constitutive relations in the continuum assumption become inadequate in accurately representing the flow. In such cases, higher order approximations such as in the Burnett equations are required for accurate solutions. Moreover, the no-slip assumption in the continuum flows is also inaccurate at rarefied conditions because there exists a slip at the gas-surface interface due to flow rarefaction. However, the NSF based methods with a slip boundary representing the gas-surface interaction in rarefied conditions can give reasonable solutions for flows with slight rarefaction, up to the Kn ≈ 0.1 . Thus, a region with the 0.01 < Kn < 0.1 is referred to as the slip regime or near-continuum. The hydrodynamic equations derived using the Chapman-Enskog theory are consistent with the Navier-Stokes equations with slip boundary conditions. But, the slip models only satisfy the gas-surface interactions of the rarefied flows whereas the first order approximation of the constitutive relations is still invalid. Hence, the NSF equations with slip models are only applicable for flows with slight rarefaction.

Maxwell [59] derived the first order velocity slip, $\vec{u}_{slip} = \vec{u} - \vec{u}_w$, on the surface based on the two types of interaction at the gas-surface interface: specular and diffuse, using the momentum accommodation coefficient. The momentum accommodation coefficient (σ_u) represents the fraction of diffuse reflection and $(1 - \sigma_u)$ represents fraction of specular reflection. Maxwell's expression for the first order slip velocity in vector form is given as:

$$\vec{u}_{slip} = -\frac{2 - \sigma_u}{\sigma_u} \frac{\lambda}{\mu} \vec{\tau} - \frac{3}{4} \frac{Pr(\gamma - 1)}{\gamma P} \vec{q}$$
(2.37)

$$\lambda = \frac{2\mu}{\rho\bar{c}} = \frac{\mu}{\rho} \sqrt{\frac{\pi}{2RT}}$$
(2.38)

$$Pr = \frac{\mu C_p}{\eta} \tag{2.39}$$

where, $\vec{\tau} = (I - \vec{n}\vec{n}) \cdot (\vec{n} \cdot \prod)$ is the tangential shear stress, $\vec{q} = \vec{Q} \cdot (I - \vec{n}\vec{n})$ is the tangential heat flux, \prod is the stress tensor at the wall; $\prod = \mu \left[\nabla \vec{u} + (\nabla \vec{u})^T - \frac{2}{3} (\nabla \cdot \vec{u}) I \right]$ (superscript T denotes transpose), and \vec{Q} is the heat flux vector at the wall, \vec{n} is a unit vector normal to the wall pointing outwards, and I is the identity tensor. Pr is the Prandtl number, γ is the ratio of specific heat, P is the gas pressure at the wall, and \bar{c} is the mean molecular speed and R is the gas constant. In the above expression 2.37, the second part represents the thermal creep. The above expression of velocity slip evaluated for a two dimensional wall using the full stress tensor in Navier-Stokes equations reduces to:

$$u_s = \frac{2 - \sigma_u}{\sigma_u} \lambda \Big(\frac{\partial u_x}{\partial n} + \frac{\partial u_n}{\partial x} \Big) + \frac{3}{4} \frac{\mu}{\rho T} \frac{\partial T}{\partial x}$$
(2.40)

where u_s is the slip component tangential to the wall, and u_n and u_x are the gas velocities normal and tangential to the wall, respectively. The second derivative term in Eq. 2.40, the so-called curvature effect: $\frac{\partial u_n}{\partial x}$, represents the gradient of wall normal velocity in the spanwise direction, which is zero for a wall without curvature and/or rotation. Lockerby et al. [60] pointed out the misapplication of the velocity slip boundary by excluding this term can ignore crucial physics in the flowfield involving boundaries with curvature and/or rotational motion. The application of the above slip boundary condition ignoring the second derivative term is still widespread and is often applied to any wall with/without the curvature.

The boundary condition for the translational temperature jump proposed by von Smoluchowski [61] that is derived based on the heat flux normal to the surface is given as:

$$T - T_w = -\frac{2 - \sigma_T}{\sigma_T} \frac{2\gamma}{(\gamma + 1)Pr} \lambda \nabla_n T = -\frac{2 - \sigma_T}{\sigma_T} \lambda_T \nabla_n T$$
(2.41)

$$\lambda_T = \frac{2\gamma}{(\gamma+1)Pr} \lambda = \frac{2}{(\gamma+1)} \frac{\eta}{\rho C_v} \sqrt{\frac{\pi}{2RT}}$$
(2.42)

where σ_T is the thermal accommodation coefficient and perfect energy exchange between the gas and the solid surface corresponds to $\sigma_T = 1$ while no energy exchange corresponds to $\sigma_T = 0$. $\nabla_n \equiv \vec{n} \cdot \nabla$, is the component of the gradient normal to the boundary surface (positive inwards). Some variations of the von Smoluchowski temperature jump condition are also present in the literature. Le et al. [62] proposed an improved von Smoluchowski temperature jump condition including the viscous heat dissipation due to the velocity slip over the surface and the results have shown better agreement with DSMC compared to the original temperature jump condition. The temperature jump condition considering the shear work due to velocity slip at the surface proposed by Le et al. is as follows:

$$T - T_w = -\frac{2 - \sigma_T}{\sigma_T} \lambda_T \nabla_n T - \frac{2 - \sigma_T}{\sigma_T} \frac{\lambda_T}{\eta} (\vec{\tau} \cdot \vec{u}_{slip})$$
(2.43)

Here, the shear work per unit area is $-(\vec{\tau} \cdot \vec{u}_{slip})$ (positive inwards) similar to $\vec{n} \cdot \vec{q}$, which is the heat conducted per unit area (positive inwards). The heat transfer through the walls should also include the viscous heat due to the slip. Thus, the heat transfer through a surface with the Fourier law of heat conduction and the viscous dissipation due to slip becomes:

$$q = -\eta \nabla_n T - (\vec{\tau} \cdot \vec{u}_{slip}) \tag{2.44}$$

Note that under the no-slip condition, the heat flux through a surface is given by the Fourier law of heat conduction alone.

At the rarefied conditions, a full accommodation of the vibrational energy to the translational energy at the wall surface boundary is not a reasonable assumption. The accommodation coefficient of the vibrational energy at a gas-surface interface is orders of magnitude lower to the translational energy accommodation coefficient. Usually an extension of Maxwell velocity slip like model, such as given in Ref. [63], is used to model the vibrational energy jump at a gas-surface interface in CFD. The vibrational energy jump at the gas-surface interface is given as:

$$\mathbf{e}_{v,g} - \mathbf{e}_{v,w} = -\frac{2 - \sigma_v}{\sigma_v} \lambda \nabla_n \mathbf{e}_{v,g}$$
(2.45)

In Ref. [64], the vibrational energy jump model by Gokcen in Ref. [63] was used with the vibrational accommodation coefficient (σ_v) of 10⁻³. Since the Fluent-NEQ solves vibrational relaxation equation for each diatomic components in air, the Eq. (2.45) is evaluated for each relaxation equations, with the same vibrational accommodation coefficient.

2.9.1 Rarefied flow over a flat plate

As a verification of the slip models in the Fluent-NEQ, the experiment by Becker [65] that investigates the rarefied argon flow over a flat plate was simulated with the Maxwell first order velocity slip and von Smoluchowski temperature jump models. The freestream conditions in the flat plate experiment is given in Table 2.3.

Table 2.3. Freestream conditions for rarefied flow over a flat plate.

V_{∞}	$1893.7 { m m/s}$
T_{∞}	$64.5~\mathrm{K}$
P_{∞}	3.73 Pa
λ_∞	$0.23 \times 10^{-3} \mathrm{m}$
T_w	292 K

Variation of velocity slip and temperature jump over the flat plate are shown in Fig. 2.8a and 2.8b, respectively. The velocity slip and temperature jump are maximum near the leading edge of the flat plate where the flat plate experiences maximum flow rarefaction. The slip effects diminishes as we move along the length of the flat plate.



Figure 2.8. Plot of (a) velocity slip and (b) temperature jump over the surface of a flat plate in rarefied flow.

Comparison of velocity slip from the Maxwell slip model and the measurements in Ref. [65] indicate that the slip models give a reasonable approximation of the slip velocity at the rarefied conditions, see Fig. 2.8a. An engineering surface will always have a surface roughness that results in the gas-surface reflection being more closer towards the diffuse reflection. Hence, even a smoothly manufactured surface will have a combination of specular and diffuse gas-surface reflection, i.e. $0 < \sigma_u < 1$. This can be seen from the comparison with the experiment measurement in Fig. 2.8a where the full momentum accommodation under-estimates the slip velocity.

Temperature jump is about 500 K near the leading edge of the flat plate, Fig. 2.8a. This shows that the temperature jump in the rarefied condition can be significant and requires the slip models to accurately represent this phenomenon. The pressure variation across the flat plate in the rarefied conditions is shown in Fig. 2.9.



Figure 2.9. Plot of surface pressure over a flat plate in rarefied flow.

Fig. 2.8a, 2.8b, and 2.9 also shows the comparison of Fluent-NEQ solution (referred to as Fluent) with the results in Ref. [66], referred to as Le (2012). The results in Fluent-NEQ is consistent with the published results in Ref. [66] and indicate a proper implementation of the slip models in Fluent-NEQ.

3. MF-CFD MODEL

The Macheret-Fridman classical impulsive model gives analytical expressions for the rate of dissociation of molecules in thermochemical nonequilibrium. The model makes some underlying assumptions that the collision of molecules can be adequately represented by classical mechanics. This is usually true for collisions at high temperatures and energies. Additionally, it assumes that the dissociation occurs through a single collision between the dissociating molecule and its collision partner. Due to the high velocity required to dissociate a molecule in a single collision, the collision is considered to be instantaneous, resulting in it being in the impulsive (hard-sphere) limit. The model also assumes that the dissociation happens through the maximum energy transfer from the collision system to the dissociating molecule, meaning the dissociation occurs only through the configuration that results in a minimum energy barrier. At last, the model assumes there are no three-body interactions between the collision partners before and after a collision.

Based on the above-mentioned assumptions, simple analytical expressions can be derived for the dissociation rates in nonequilibrium at the impulsive limit. Despite the model simplistically treating the molecular collisions, it reproduces some of the important physics of dissociation in nonequilibrium. The MF model promotes the dissociation for molecules with high vibrational excitation, thus preserving the vibrationally favoring dissociation in nonequilibrium. The model includes the rotational contribution to the dissociation of molecules as well. Furthermore, the MF model differentiates the dissociation mechanism into dissociation from a high vibrational level and dissociation from a low vibrational level. This helps to model the critical contribution of translational energy to the dissociation of molecules at a low vibrational level (as T becomes larger and T_v remains low), the mechanism that is often not represented by other vibration-dissociation models. Additionally, the MF model also provides the analytical expression for the loss of average vibrational energy due to dissociation, which is referred to as the preferential vibration-dissociation coupling.

In terms of limitations of the MF model, the model is restricted to the dissociation of diatomic molecules. Also, the model in its current form only represents the dissociation of neutral species, since it does not take account of radicals, ions, or the degenerate electronic states of molecules. Despite its limitations, it is quite commendable how much detail of the dissociation in nonequilibrium is embraced by the MF model and the model warrants further investigation and development.

Taking into account the above mentioned assumptions, a general form of MF model, can be derived for heteronuclear molecules by revisiting the classical impulsive theory.





Figure 3.1. Collision geometry for (a) diatom-atom and (b) diatom-diatom collisions.

The collision geometry for the diatom-atom and diatom-diatom collisions are shown in Fig. 3.1. The molecule AB is the dissociating molecule with atom C as the collision partner for diatom-atom collision and molecule CD as the collision partner for the diatom-diatom collision. A collision plane xy was defined as the right-handed coordinate system using atoms A, B, and C with y-axis in the direction of BC.

The velocities of molecules AB and CD in the center-of-mass frame are v and u respectively, in [m/s]. The direction of the velocity u is defined by the polar angle γ_1 and the azimuthal angle γ_2 , in [rad]. The magnitude of the vibrational velocity for molecule AB is $v_0 \cos \phi_0$ with phase angle ϕ_0 and the magnitude of the vibrational velocity for molecule CD is $v_1 \cos \phi_1$ with phase angle ϕ_1 (in a diatom-diatom collision). The phase angles ϕ_0 and ϕ_1 are assumed to be distributed uniformly between 0 and 2π representing a harmonic motion. The direction of the vibrational motion of molecule AB is given by angle θ . For CD molecule, the polar and the azimuthal angles for the vibrational velocity are β_1 and β_2 respectively. v_r is the rotational velocity of the molecule AB perpendicular to the vibrational velocity with polar angle β . The rotational velocity of the CD molecule v'_r is defined using two reference planes \vec{c}_{ref1} and \vec{c}_{ref2} such that \vec{c}_{ref1} is in the collision plane xy and is perpendicular to the vibrational velocity v_1 , whereas \vec{c}_{ref2} is perpendicular to both \vec{c}_{ref1} and v_1 . Thus, the direction of the rotational velocity is determined by the angle δ that is the angle between v'_r and \vec{c}_{ref2} . The collision geometry defined here (in Fig. 3.1) is based on the work of Luo et al. in Ref. [32].

The vibrational energy of the molecules AB and CD are denoted as E_v and E'_v respectively, in [K]. The rotational energy of the molecules AB and CD are denoted as E_r and E'_r respectively. E_t denotes the collision translational energy. The definition of energies are as follows:

$$E_v = 2\mu_1 v_0^2, \quad E'_v = 2\mu_2 v_1^2, \quad E_r = 2\mu_1 v_r^2, \quad E'_r = 2\mu_2 v_r'^2, \quad E_t = \frac{(m_A + m_B)^2 v^2}{2\mu}.$$
 (3.1)

Here, μ_1 and μ_2 are the reduced masses of molecules AB and CD respectively, in [kg]. The reduced mass μ_2 becomes the mass of atom C for diatom-atom collision. μ is the reduced mass of the whole collision system. Denoting m_A , m_B , m_C , and m_D as the mass of atom A, B, C, and D respectively in [kg], the reduced masses are:

$$\mu_{1} = \frac{m_{A}m_{B}}{m_{A} + m_{B}}, \quad \mu_{2} = \frac{m_{C}m_{D}}{m_{C} + m_{D}},$$

$$\mu = \begin{cases} \frac{(m_{A} + m_{B})m_{C}}{m_{A} + m_{B} + m_{C}} & \text{diatom-atom collisions} \\ \frac{(m_{A} + m_{B})(m_{C} + m_{D})}{m_{A} + m_{B} + m_{C} + m_{D}} & \text{diatom-diatom collisions.} \end{cases}$$

$$(3.2)$$

The derivation of macroscopic rates of dissociation using the classical impulsive theory proceeds in the following manner. (1) At first, solve the binary elastic collision between the colliding atoms B and C to determine the post-collision vibrational energy of the dissociating molecule AB. Since the model assumes binary interactions, the components of velocities are allowed to change in the direction of B and C atoms only. (2) The next step is to solve for the minimum collision translation energy E_t (will be referred to as threshold function), which results in the post-collision vibrational energy of dissociating molecule AB to be equal to its dissociation energy. (3) Next, determine the threshold line representing the optimum collision configuration that results in the maximum energy transfer from the collision translation energy to the post vibrational energy of the dissociating molecule AB. (4) The dissociation probability is then calculated utilizing the *Taylor expansion* of the threshold function near the optimum configuration. (5) Finally, derive the multi-temperature macroscopic nonequilibrium dissociation rates by integrating the probability of the minimum threshold configuration (dissociation probability) with the distribution of translational, rotational, and vibrational energies.

The dissociation rates for diatom-atom and diatom-diatom collision pairs are represented separately because of the additional degrees of freedom in a diatom-diatom collision. The rotational and vibrational energy of the collision partner (CD) contribute to the dissociation, hence the rates are different for diatom-atom and diatom-diatom collision pairs.

3.1.1 Diatom-Atom collisions

The multi-temperature dissociation rate expressions for the diatom-atom collisions involving heteronuclear molecules were found to be similar to the rates of homonuclear molecules. The derivation of the dissociation rates follows the steps highlighted above. The threshold function for the diatom-atom collision obtained by solving the two body elastic collision between atom B and C in the dissociation reaction of $AB + C \longrightarrow A + B + C$ is as follows:

$$E_t = G = \frac{\mu/\mu_1}{4\cos^2\gamma_1\cos^2\gamma_2} \left\{ \frac{\sqrt{D - E_v \sin^2\phi_0} + \sqrt{E_v}\cos\phi_0}{\cos\theta m_C/(m_B + m_C)} - \frac{2\mu_1}{m_B} \left[\sqrt{E_v}\cos\phi_0\cos\theta + \sqrt{E_r}\cos\beta\sin\theta \right] \right\}^2.$$
(3.3)

Here, G is the minimum collision translational energy required for the dissociation of the molecule AB. As mentioned before, it is obtained by setting the post-collision vibrational energy of molecule AB equal to its dissociation energy (D). The above threshold function can

be directly used in DSMC to model dissociation through classical impulsive theory without calculating the dissociation probability, see Ref. [32]. The threshold function obtained here is the same as in Ref. [32].

For simplification, the contribution of the pre-collision rotational energy is represented by replacing the dissociation energy (D) by the effective dissociation energy (D_{ef}) and removing the last term in the Eq. (3.3). For a rotating molecule, the effective dissociation energy D_{ef} is less than $D - E_r$ due to the angular momentum conservation known as the centrifugal barrier effects [27]. An estimation of the interaction energy based on long range potential $V(r) = -bD(R_{eq}/r)^6$, where R_{eq} is the equilibrium distance of molecule bond, r is the intermolecular distance, and b is the Lennard-Jones parameter for the dissociating molecule, usually taken as b = 2, gives:

$$D_{\rm ef} = D - E_r + \frac{2E_r^{3/2}}{3\sqrt{3bD}} .$$
 (3.4)

The study in Ref. [29] has demonstrated the importance of retaining this vibrational-rotational (VR) effects in the dissociation.

The threshold function with the simplification becomes:

$$E_t = G = \frac{\mu/\mu_1}{4\cos^2\gamma_1\cos^2\gamma_2} \left\{ \frac{\sqrt{D_{\rm ef} - E_v\sin^2\phi_0} + \sqrt{E_v}\cos\phi_0}{\cos\theta m_C/(m_B + m_C)} - \frac{2\mu_1}{m_B} \left[\sqrt{E_v}\cos\phi_0\cos\theta \right] \right\}^2.$$
(3.5)

An optimum configuration of the threshold function is obtained by setting all the partial derivative of the function G with respect to the phase angles to zero i.e. $\partial G/\partial \gamma_i = 0$. The optimum configuration (threshold line) turns out to be:

$$\gamma_1 = \gamma_2 = \theta = 0,$$

$$\cos \phi = \begin{cases} -1 & \text{if } E_v \le \alpha D_{\text{ef}} \\ -\left(\frac{\alpha}{1-\alpha} \frac{D_{\text{ef}} - E_v}{E_v}\right)^{1/2} & \text{if } E_v > \alpha D_{\text{ef}}. \end{cases}$$
(3.6)

The expression in Eq. (3.6) is same as in Ref. [27] (Eq. (15)) obtained for the special case of homonuclear molecule. However, the definition of the parameter α here is more general and is given as:

$$\alpha = \left(1 - \frac{2\mu_1}{m} \frac{M}{m+M}\right)^2. \tag{3.7}$$

Where $m \in [m_B, m_A]$ and $M \in [m_C]$ are based on the optimum collision arrangement. The optimum arrangement is determined by a configuration that results in the smallest α parameter, Eq. (3.7). For diatom-atom collision, there are two possible collision arrangements: (a) A-B + C and (b) B-A + C, where the colliding atoms are B and C in configuration-(a) and A and C in configuration-(b). It is trivial to show that the α parameter here in Eq. (3.7) will reduce to $\alpha = (m/(m+M))^2$ that is given in Ref. [27] for a homonuclear molecule i.e. $m_A = m_B$.

Using the definition of the parameter α , the threshold function G and threshold line F are further reduced to:

$$E_{t} = \frac{1}{(1-\alpha)\cos^{2}\gamma_{1}\cos^{2}\gamma_{2}} \left\{ \frac{\sqrt{D_{ef} - E_{v}\sin^{2}\phi_{0}} + \sqrt{E_{v}}\cos\phi_{0}}{\cos\theta} - (1-\sqrt{\alpha})\sqrt{E_{v}}\cos\phi_{0}\cos\theta \right\}^{2}, \qquad (3.8a)$$

$$E_t = F(E_v) = \begin{cases} \frac{\left(\sqrt{D_{\rm ef}} - \sqrt{\alpha E_v}\right)^2}{1 - \alpha} & \text{if } E_v \le \alpha D_{\rm ef} \\ D_{\rm ef} - E_v & \text{if } E_v > D_{\rm ef}. \end{cases}$$
(3.8b)

The threshold function and the threshold line obtained here are same as in Ref. [27] with only difference being the definition of the parameter α known as the mass fraction.

The full derivation of the reaction rates for diatom-atom collisions is present in Ref. [27] which was later revisited in Ref. [29] with corrections to some minor numerical mistakes in Ref. [27]. Since, the threshold function and the threshold line obtained here are same as in Ref. [27] and the mass fraction parameter α is independent of the integrating variables, the full derivation is not presented here, as it will merely be a repetition. For full derivation, refer to Ref. [27] and Ref. [29].

The multi-temperature reaction rate for low vibrational level when $E_v \leq \alpha D_{ef}$ is as follows:

$$k_l(T, T_v) = AT^n \times L \exp\left(-\frac{D}{T_a} + \Delta D\left(\frac{1}{T_a} - \frac{1}{T}\right)\right), \qquad (3.9a)$$

$$L = \frac{\sqrt{1-\alpha}}{\pi^{3/2}} \sqrt{\frac{D}{D^*}} \left(\frac{T}{D}\right)^{1-n} \left(1 + \frac{5(1-\alpha)T}{2D^*}\right) \left(12\pi b\alpha(1-\alpha)\frac{D}{T}\right)^{1/2}.$$
 (3.9b)

Where, A and n are the Arrhenius rate coefficients, T_a is the average temperature defined as:

$$T_a = (1 - \alpha)T + \alpha T_v . \tag{3.10}$$

 D^* is the approximated value of effective dissociation energy (D_{ef}) under the assumption of very small value of α and

$$D^* = D - \Delta D = D - 3b\alpha^2 D$$
. (3.11)

At high vibrational levels, the dissociation mainly occurs from the population of highest vibrational excitation. Thus for $E_v > \alpha D_{ef}$, the rates are calculated based on the ratio

of nonequilibrium-to-equilibrium population ratio rather than from dissociation probability. Hence, the dissociation rate for $E_v > \alpha D_{ef}$ is given as

$$k_h(T, T_v) = AT^n \times (1 - L) \frac{1 - \exp(-\Theta_v/T_v)}{1 - \exp(-\Theta_v/T)} \exp\left(-\frac{D}{T_v}\right).$$
(3.12)

Where, Θ_v is the characteristic vibrational temperature of the dissociating molecule.

The nonequilibrium multi-temperature rates will reduce to Arrhenius rates under the equilibrium condition of $T = T_v$.

3.1.2 Diatom-Diatom collisions

The threshold function for the diatom-diatom collision obtained by solving the two body elastic collision between atom B and C in the dissociation reaction of $AB + CD \longrightarrow A + B + CD$ is as follows:

$$E_{t} = G = \frac{\mu/\mu_{1}}{4\cos^{2}\gamma_{1}\cos^{2}\gamma_{2}} \left\{ \frac{\sqrt{D_{ef} - E_{v}\sin^{2}\phi_{0}} + \sqrt{E_{v}}\cos\phi_{0}}{\cos\theta m_{C}/(m_{B} + m_{C})} - \frac{2\mu_{1}}{m_{B}} \left[\sqrt{E_{v}}\cos\phi_{0}\cos\phi_{0}\cos\theta \right] - \frac{2\sqrt{\mu_{1}\mu_{2}}}{m_{C}} \left[\sqrt{E_{r}'}(\cos\delta\cos\beta_{2}\sin\beta_{1} + \sin\delta\sin\beta_{2}) - \sqrt{E_{v}'}\cos\phi_{1}\cos\beta_{1}\cos\beta_{2} \right] \right\}^{2}.(3.13)$$

The optimum configuration to the threshold function in diatom-diatom collision is:

$$\gamma_1 = \gamma_2 = \theta = 0, \quad \phi_1 = 0, \quad \beta_1 = 0,$$

$$\beta_2 = \pi - \tan^{-1} \left(\sqrt{E'_r / E'_v} \right), \quad \delta = \pi/2,$$

$$\cos \phi = \begin{cases} -1 & \text{if } E_v \le \alpha D_{\text{ef}} \\ -\left(\frac{\alpha}{1-\alpha} \frac{D_{\text{ef}} - E_v}{E_v}\right)^{1/2} & \text{if } E_v > \alpha D_{\text{ef}}. \end{cases}$$
(3.14)

Here, the mass fraction parameter α is same as in Eq. (3.7) with $m \in [m_B, m_A]$ and $M \in [m_C, m_D]$ based on the optimum collision arrangement. For diatom-diatom collisions, there are 4 different possible collision arrangements; (a) A-B + C-D, (b) A-B + D-C, (c) B-A +

C-D, and (d) B-A + D-C. m and M depend on the configuration that results in the minimum value of the parameter α .

The threshold function can be further reduced to:

$$G = \frac{C_1}{(1-\sqrt{\alpha})\cos^2\gamma_1\cos^2\gamma_2} \left(\frac{\sqrt{D_{\rm ef} - E_v\sin^2\phi_0} + \sqrt{E_v}\cos\phi_0}{\cos\theta} - (1-\sqrt{\alpha})\sqrt{E_v}\cos\phi_0\cos\theta - C_2\sqrt{\sqrt{\alpha}(1-\sqrt{\alpha})} \left[\sqrt{E_r'}(\cos\delta\cos\beta_2\sin\beta_1 + \sin\delta\sin\beta_2) - \sqrt{E_v'}\cos\phi_1\cos\beta_1\cos\beta_2 \right] \right)^2, \quad (3.15a)$$

$$C_1 = \frac{\mu\mu_1}{m^2} \frac{1}{1 - \sqrt{\alpha}} \qquad C_2 = \sqrt{\frac{1 - \sqrt{\alpha}}{\sqrt{\alpha}}} \sqrt{\frac{\mu_2}{\mu_1}} \frac{m}{M}$$
 (3.15b)

The two heteronuclear parameters: C_1 and C_2 are defined in such a way that for homonuclear molecules these parameters simply reduce to unity.

3.1.2.1 Dissociation rates at low vibrational level

The threshold line corresponding to the optimum configuration, Eq. (3.14), at low vibration level $E_v \leq \alpha D_{ef}$ is:

$$E_{t} = F(E_{v}) = \frac{C_{1}}{(1 - \sqrt{\alpha})} \left(\sqrt{D_{\text{ef}}} - \sqrt{\alpha E_{v}} - C_{2} \sqrt{\sqrt{\alpha}(1 - \sqrt{\alpha})} \sqrt{E_{r}' + E_{v}'} \right)^{2}.$$
 (3.16)

As mentioned before, the probability of dissociation is obtained by the *Taylor expansion* of the threshold function near the optimum configuration. Here, the threshold function is expanded up to the second order as:

$$E_t = F(E_v) + \frac{1}{2} \sum_{i,j} G_{ij} \Delta \gamma_i \Delta \gamma_j . \qquad (3.17)$$

The envelope $S(\gamma_1, \gamma_2, ..., \gamma_n)$ with the threshold energy equal to E_t form a n-dimensional ellipsoid. The ratio of the volume of the multidimensional ellipsoid $V(E_t, E_v)$ and the volume of the entire accessible phase space corresponding to the full range of variation of the angular and phase variable will give the probability of reaction.

The second order derivatives G_{ij} at the optimum configuration (Eq. (3.14)) are as follows:

$$\begin{aligned}
G_{\gamma_{1}\gamma_{1}} &= G_{\gamma_{1}\gamma_{1}} = 2F, \\
G_{\theta\theta} &= 2\left(\sqrt{D_{ef}} - (2 - \sqrt{\alpha})\sqrt{E_{v}}\right) \left(\frac{FC_{1}}{1 - \sqrt{\alpha}}\right)^{1/2}, \\
G_{\phi_{0}\phi_{0}} &= 2\left(\sqrt{\alpha D_{ef}} - \sqrt{E_{v}}\right) \left(\frac{FE_{v}C_{1}}{(1 - \sqrt{\alpha})D_{ef}}\right)^{1/2}, \\
G_{\phi_{1}\phi_{1}} &= G_{\beta_{1}\beta_{1}} = 2E_{v}' \left(\frac{F\sqrt{\alpha}C_{1}C_{2}^{2}}{E_{r}' + E_{v}'}\right)^{1/2}, \\
G_{\beta_{2}\beta_{2}} &= 2\left(F\sqrt{\alpha}C_{1}C_{2}^{2}(E_{r}' + E_{v}')\right)^{1/2}, \\
G_{\delta\delta} &= 2E_{r}' \left(\frac{F\sqrt{\alpha}C_{1}C_{2}^{2}}{E_{r}' + E_{v}'}\right)^{1/2}.
\end{aligned}$$
(3.18)

Here, all the cross derivatives terms are zero. Various derivatives in Eq. (3.18) are zero for $E_v \to D_{ef}$ and $E_v \to \alpha D_{ef}$ and will result in singularities in the reaction probability. Also, integration of the probability over E'_r and E'_v in the region $T_v \leq T_r \leq T_t$ shows that the integral is determined in the vicinity of $E'_v = 0$. Here, these singularities are treated in the same manner as in Ref. [27] and some derivatives are dropped while calculating the dissociation probability. These singularities occur when the scattering becomes independent of the variations in some coordinates. Hence, the overall degrees of freedom is reduced while calculating the probability of the minimum threshold configuration [27].

The resulting dissociation probability for low vibration level $E_v \leq \alpha D_{ef}$ is:

$$P = \frac{8(E_t - F)^{5/2}}{15\pi^3 C_1^{3/4} C_2 \alpha^{1/4} \left(1 - \sqrt{\alpha}\right)^{-1/4} F^{7/4} \sqrt{E_r' \left(\sqrt{D_{\rm ef}} - (2 - \sqrt{\alpha})\sqrt{E_v}\right)} \quad \text{for } E_v \le \alpha D_{\rm ef}.$$
(3.19)

In order to reduce the complexity of calculating the reaction rates, the VR effects are ignored for now and replace D_{ef} simply by D. The dissociation probability is then integrated over the translational energy E_t with a Maxwellian distribution $f_{T_t}(E_t)$ to obtain macroscopic rates as a function of rotational and vibrational energy, $k_l(E_v, E'_r, T_t)$.

$$k_{l}(E_{v}, E_{r}', T_{t}) = Z \int_{F}^{\infty} P \frac{E_{t}}{T_{t}} \exp\left[-\frac{E_{t}}{T_{t}}\right] d\frac{E_{t}}{T_{t}}$$

$$= \frac{\exp\left[-\frac{F}{T_{t}}\right] Z T_{t}^{3/2} (2F + 7T_{t})}{2\pi^{5/2} C_{1}^{3/4} C_{2} \alpha^{1/4} \left(1 - \sqrt{\alpha}\right)^{-1/4} F^{7/4} \sqrt{E_{r}' \left(\sqrt{D} - (2 - \sqrt{\alpha})\sqrt{E_{v}}\right)}.$$
(3.20)

Here, Z is the gas-kinetic collision rate coefficient.

The integration over the rotational energy E'_r with the Maxwellian distribution, in order to determine the dissociation rate as a function of vibrational energy such that $k_l(E_v, T_r, T_t) = \int_{E'_r} k_l(E_v, E'_r, T_t) f(E'_r) dE'_r$, is performed using the steepest descent method as the integration is basically determined at the vicinity of point maximizing the exponent:

$$\exp\left[-\frac{F}{T_t} - \frac{E_r'}{T_r}\right].$$
(3.21)

The exponent in Eq. (3.21) has a maxima at the rotational energy of

$$E_r^{\prime*} = \frac{C_1^2 C_2^2 \sqrt{\alpha} T_r^2 \left(\sqrt{D} - \sqrt{\alpha} E_v\right)^2}{\left(1 - \sqrt{\alpha}\right) \left(T_t + C_1 C_2^2 \sqrt{\alpha} T_r\right)^2} \,. \tag{3.22}$$

Thus, the dissociation rate as a function of vibrational energy, assuming rotational equilibrium $T_r = T_t = T$, becomes¹:

$$k_{l}(E_{v},T) = \exp\left[-\frac{C_{1}\left(\sqrt{D}-\sqrt{\alpha E_{v}}\right)^{2}}{(1-\sqrt{\alpha})\left(1+C_{1}C_{2}^{2}\sqrt{\alpha}\right)T}\right] \times \frac{Z\left(1-\sqrt{\alpha}\right)\left(1+C_{1}C_{2}^{2}\sqrt{\alpha}\right)T\left(7T\left(1-\sqrt{\alpha}\right)\left(1+C_{1}C_{2}^{2}\sqrt{\alpha}\right)^{2}+2C_{1}\left(\sqrt{D}-\sqrt{\alpha E_{v}}\right)^{2}\right)}{\pi^{2}C_{1}^{5/2}C_{2}\alpha^{1/4}\sqrt{\sqrt{D}-(2-\sqrt{\alpha})\sqrt{E_{v}}}\left(\sqrt{D}-\sqrt{\alpha E_{v}}\right)^{7/2}} (3.23)$$

The steepest descent approximate integration method, also known as saddle-point method, utilized in this work was reviewed in Ref. [67].

 $\overline{}^{1}\uparrow \text{Here, } F = F(E'_{r} = E'^{*}_{r}, \ E'_{v} = 0) \text{ in Eq. } (3.16).$

The next step into the derivation of macroscopic rates is to integrate the rate as a function of vibrational energy, $k_l(E_v, T)$, over the quasi Boltzmann distribution of vibrational energy with vibrational temperature T_v . The integration is again carried out by the steepest descent method and the exponent:

$$\exp\left[-\frac{C_1\left(\sqrt{D}-\sqrt{\alpha E_v}\right)^2}{\left(1-\sqrt{\alpha}\right)\left(1+C_1C_2^2\sqrt{\alpha}\right)T}-\frac{E_v}{T_v}\right],\tag{3.24}$$

has a maxima at the vibrational energy of:

$$E_{v}^{*} = \alpha D \left(\frac{T_{v}}{(1 - \sqrt{\alpha}) (1/C_{1} + C_{2}^{2} \sqrt{\alpha}) T + \alpha T_{v}} \right)^{2}.$$
 (3.25)

Here, the original form of the steepest descent method will result in an incorrect preexponent factor at the limiting case of $T_v \to 0$. So, the integration over the vibrational energy is treated in the same manner as in Ref. [27]; by preserving the most important exponent factor from the steepest descent method and calculating the preexponent at the limit of $T_v \to 0$. The exponent of the rate turns out to be:

$$\exp\left[-\frac{D}{T_a}\right],\tag{3.26a}$$

$$T_a = \left(1 - \sqrt{\alpha}\right) \left(1/C_1 + C_2^2 \sqrt{\alpha}\right) T + \alpha T_v.$$
(3.26b)

Here, T_a is referred to as the average temperature. The average temperature obtained here for diatom-diatom collisions is slightly different to that in diatom-atom collision (Eq. (3.10)). However, the definition of the average temperature from Eq. (3.26b) can be used as a general expression for T_a with the parameters $C_1 = 1$ and $C_2 = 1$ for diatom-atom collisions, since these parameters are only relevant for diatom-diatom collisions. The preexponent factor evaluated at limit $T_v \to 0$ becomes:

$$\frac{k_l(T_v,T)}{\exp\left[-\frac{D}{T_a}\right]} = \lim_{T_v \to 0} \frac{Z\left(1-\sqrt{\alpha}\right)\left(1+C_1C_2^2\sqrt{\alpha}\right)T\left(7T\left(1-\sqrt{\alpha}\right)\left(1+C_1C_2^2\sqrt{\alpha}\right)^2+2C_1\left(\sqrt{D}-\sqrt{\alpha E_v^*}\right)^2\right)}{\pi^2 C_1^{5/2} C_2 \alpha^{1/4} \sqrt{\sqrt{D}-(2-\sqrt{\alpha})\sqrt{E_v^*}}\left(\sqrt{D}-\sqrt{\alpha E_v^*}\right)^{7/2}} \\
= \frac{2Z\left(1-\sqrt{\alpha}\right)\left(1+C_1C_2^2\sqrt{\alpha}\right)T\left(1+\frac{7T\left(1-\sqrt{\alpha}\right)\left(1+C_1C_2^2\sqrt{\alpha}\right)^2}{2C_1D}\right)}{\pi^2 C_1^{3/2} C_2 \alpha^{1/4} D}.$$
(3.27)

Finally, the macroscopic dissociation rate at low vibrational level results in the following:

$$k_{l}(T_{v},T) = \exp\left[-\frac{D}{T_{a}}\right] \frac{2\left(1-\sqrt{\alpha}\right)\left(1+C_{1}C_{2}^{2}\sqrt{\alpha}\right)}{\pi^{2}C_{1}^{3/2}C_{2}\alpha^{1/4}}Z\left(\frac{T}{D}\right) \\ \times \left(1+\frac{7T\left(1-\sqrt{\alpha}\right)\left(1+C_{1}C_{2}^{2}\sqrt{\alpha}\right)^{2}}{2C_{1}D}\right).$$
(3.28)

In order to include the VR effects— contribution of rotational energy and centrifugal barrier effects on dissociation, the rate equations need to be derived using the effective dissociation D_{ef} instead of D. After applying the steepest descent method to calculate the integration over the rotational energy E_r , the rates turned out to be similar as in Eq. (3.28) with D replaced simply by D^* and with extra exponent and preexponent terms. The resulting dissociation rate with VR effects becomes:

$$k_{l}(T_{v},T) = \frac{2\left(1-\sqrt{\alpha}\right)\left(1+C_{1}C_{2}^{2}\sqrt{\alpha}\right)}{\pi^{2}C_{1}^{3/2}C_{2}\alpha^{1/4}}Z\left(\frac{T}{D^{*}}\right)\left(1+\frac{7T\left(1-\sqrt{\alpha}\right)\left(1+C_{1}C_{2}^{2}\sqrt{\alpha}\right)^{2}}{2C_{1}D^{*}}\right)$$
$$\times \left(12\pi b\left(1-\sqrt{\alpha}\right)\left(1/C_{1}+C_{2}^{2}\sqrt{\alpha}\right)\left(1-\left(1-\sqrt{\alpha}\right)\left(1/C_{1}+C_{2}^{2}\sqrt{\alpha}\right)\right)\frac{D}{T}\right)^{1/2}$$
$$\times \exp\left(-\frac{D}{T_{a}}+\Delta D\left(\frac{1}{T_{a}}-\frac{1}{T}\right)\right), \qquad (3.29a)$$

$$D^* = D - \Delta D = D - 3b \left(1 - \left(1 - \sqrt{\alpha} \right) \left(1/C_1 + C_2^2 \sqrt{\alpha} \right) \right)^2 D.$$
 (3.29b)

Rather than attempting to calculate the gas kinetic collision rate coefficient (Z) through a collision model, the parameter Z is substituted in terms of Arrhenius preexponent factor, Eq. (3.30). It ensures that the rates will reduce to Arrhenius rates at equilibrium $(T = T_v)$, as it should be.

$$AT^{n} = Z\left(\frac{D}{T}\right)^{1/2-n}.$$
(3.30)

Thus, the final expression for multi-temperature rate at low vibrational level is as follows:

$$k_l(T, T_v) = AT^n \times L \exp\left(-\frac{D}{T_a} + \Delta D\left(\frac{1}{T_a} - \frac{1}{T}\right)\right), \qquad (3.31a)$$

$$L = \frac{2(1-\sqrt{\alpha})(1+C_1C_2^2\sqrt{\alpha})}{\pi^2 C_1^{3/2}C_2\alpha^{1/4}} \left(\frac{D}{D^*}\right) \left(\frac{T}{D}\right)^{3/2-n} \left(1+\frac{7T(1-\sqrt{\alpha})(1+C_1C_2^2\sqrt{\alpha})^2}{2C_1D^*}\right) \times \left(12\pi b\left(1-\sqrt{\alpha}\right)\left(1/C_1+C_2^2\sqrt{\alpha}\right)\left(1-(1-\sqrt{\alpha})\left(1/C_1+C_2^2\sqrt{\alpha}\right)\right)\frac{D}{T}\right)^{1/2}.$$
(3.31b)

The expression for the dissociation rates at low vibrational level in diatom-diatom collisions for general (heteronuclear) molecules will reduce to the rates for homonuclear molecules with the parameters $C_1 = 1$ and $C_2 = 1$. The rates obtained here are similar to that in Refs. [27], [29] but with a difference in exponent of the parameter α in denominator of the L-function. The L-function in in Refs. [27], [29] have $\alpha^{3/4}$, whereas the correct form should have $\alpha^{1/4}$. The mass fraction parameter α is usually very small for most collisions in air (for eg. $\alpha \sim 0.25$, for $N_2 + N_2$ collisions) so, the expressions in Refs. [27], [29] will overpredict the reaction rates by a factor of ~ 2 .

3.1.2.2 Dissociation rates at high vibrational level

The dissociation rate at high vibrational level for $E_v > D_{ef}$ in diatom-diatom collisions remain same as in diatom-atom collisions and is given as:

$$k_h(T, T_v) = AT^n \times (1 - L) \frac{1 - \exp(-\Theta_v/T_v)}{1 - \exp(-\Theta_v/T)} \exp\left(-\frac{D}{T_v}\right).$$
(3.32)

3.1.2.3 Energy removed by dissociation reaction

The average vibrational energy removed by the dissociation reaction, in [K], can be represented as:

$$E_v^{rem} = \frac{\alpha D^* (T_v/T_a)^2 k_l + \hat{D}k_h}{k_l + k_h} .$$
(3.33)

In Ref. [27], it has been shown that the contribution of rotational energy to the dissociation diminishes at a high vibrational level in the region of $T_r \leq T_t$. Thus, Eq. (3.33) predicts that the average energy removed in a dissociation from the high vibrational level is almost equal to the dissociation energy i.e. $\hat{D} \approx D$. The accuracy of this assumption of $\hat{D} \approx D$ is evaluated in the next section. The average vibrational energy removed by a dissociation reaction with diatom-atom collision is also given by the same expression as in Eq. (3.33).

3.2 Validation of the MF-CFD Model

For the validation of the MF-CFD model, some of the comparisons of MF nonequilibrium dissociation rates with QCT data were given in Ref. [29]. The comparisons were for the collision pairs: $N_2 + O$, $N_2 + N$, $O_2 + O$, $N_2 + N_2$, and $O_2 + O_2$. However, a minor mistake has been identified in the dissociation rates for the diatom-diatom collisions in Ref. [29], so the comparisons for $N_2 + N_2$ and $O_2 + O_2$ collision pairs are reproduced with the correct forms in this work.

The nonequilibrium factor by the MF-CFD model for $N_2 + N_2$ collision was calculated using the equilibrium reaction rates given in Ref. [13]. Figure 3.2 shows a good agreement of the MF-CFD model with QCT data for the given range of vibrational temperature. At a low vibrational level, it can be seen that the MF-CFD model predicts the nonequilibrium factor to be lower than the SS interpolation formula fitted to QCT data for low translational temperature.

The QCT data for $O_2 + O_2$ reaction pair were obtained from Ref. [68] for singlet and quintet spin states of $O_2 + O_2$ interaction. The equilibrium rate coefficients for this reaction were taken from Ref. [22]. Considering the QCT data has an uncertainty factor of ~ 3









(or higher) [29] for low vibrational temperatures in general, the MF-CFD shows very good agreement with the QCT data, evident in Fig. 3.3.

Looking at the nonequilibrium factors by Park's two-temperature model ($\alpha_p = 0.7$) in Fig. 3.2 and 3.3, the Park model behaves reasonably well near the equilibrium. However, the Park model shows a large deviation from QCT and MF-CFD rates in strong nonequilibrium for both vibrationally cold ($T_v < T$) and vibrationally hot ($T_v > T$) conditions.

The nonequilibrium factors by the *two-temperature Kuznetsov* model [24], [25] are also shown in Fig. 3.2 and 3.3. The two-temperature Kuznetsov model is given as:

$$k_f^{Kuznetsov}(T, T_v) = AT^n \frac{1 - \exp(-\Theta_v/T_v)}{1 - \exp(-\Theta_v/T)} \exp\left(E_v^{**}\left(\frac{1}{T} - \frac{1}{T_v}\right)\right) \exp\left(-\frac{D}{T}\right), \quad (3.34)$$

where, E_v^{**} is the threshold energy in anharmonic oscillator assumption below which the vibrational distribution is nonequilibrium and above which the vibrational distribution is in equilibrium with gas temperature (*T*). Here, the threshold energy is $E_v^{**} = 0.7D$ (Ref. [24]). Note that, under the assumption that vibration-vibration relaxation occurs very fast such that it results in the vibrational distribution to be Boltzmann with respect to T_v , the Kuznetsov model (for $E_v^{**} = D$) reduces to the k_h^{MF-CFD} , Eq. (3.12, 3.32)².

The Kuznetsov model behaves reasonably well near the equilibrium and vibrationally hot conditions, compared to Park's model. However, at vibrationally cold conditions, that is usually encountered behind a strong shock, the Kuznetsov model suppresses the dissociation by a large amount. It is because the Kuznetsov model is derived based on the assumption that dissociation occurs only through the upper vibrational levels for anharmonic oscillators. Unlike the MF-CFD model, the Kuznetsov model fails to represent the contribution of the translational-rotational energy to dissociation when vibrational excitation is low i.e. in a strong vibrational nonequilibrium ($T_v \rightarrow 0$). It is a limitation of Park's model as well.

3.2.1 Mean vibrational energy removed in dissociation

Another important aspect of the MF-CFD model is the prediction of average vibrational energy removed in a dissociation reaction. Figure 3.4 shows a comparison of the average

² \uparrow The *L*-function in Eq. (3.12, 3.32) ensures that the MF-CFD rates satisfy equilibrium (rates) for $T = T_v$.

vibrational energy removed in some important dissociation reactions predicted by the MF-CFD model, Eq. (3.33), to the available QCT data (N₂ + N₂: Ref. [13], N₂ + N: Ref. [12], $O_2 + O_2$: Ref. [69], and $O_2 + O$: Ref. [14]).



Figure 3.4. Comparison of average vibrational energy removed in a dissociation predicted by the MF-CFD model with QCT data for various dissociation reactions.

Evident from the QCT data for various dissociation reactions, the average vibrational energy removed in dissociation for high vibrational excitation decreases with the increase in the translational-rotational temperature and it is lower than the dissociation energy of the dissociating molecule (D). This phenomenon is represented by the MF-CFD model but the influence of translational-rotational temperature at a high vibrational level is underrepresented when the energy removed from the high vibrational region is assumed to be equal to the dissociation energy i.e. $\hat{D} \approx D$, originally given in Ref. [27]. Here, the author proposes the energy removed in high vibrational level to be $\hat{D} \approx D - T$ [K] i.e. the average vibrational energy removed in dissociation for high vibrational level comes from the vibrational level that is below the dissociation energy by the average kinetic energy of the molecule, k_bT , where k_b is the Boltzmann constant ($k_b = 1.38064852 \times 10^{-23}$ [J/K]). This form was previously proposed by Park in Ref. [70] to represent the average vibrational energy removed in a dissociation reaction. The MF-CFD prediction of the average vibrational energy removed in a dissociation reaction with $\hat{D} \approx D - T$ in Eq. (3.33) is also shown in Fig. 3.4. The prediction by the MF-CFD is substantially improved with this form when compared to the QCT data, at high vibrational temperature as well as in equilibrium, shown as E_v^{rem*} in Fig. 3.4. Although the influence of the translational-rotational energy to the dissociation at a high vibrational level is simplified as $\hat{D} \approx D - T$, the MF-CFD model shows improvements at high translational-rotational temperature. This is an important improvement as one expects the impulsive model to be more accurate at high translational-rotational temperature.

Furthermore, the MF-CFD model shows that the average vibrational energy removed in a dissociation reaction at a low vibrational level ($T_v \ll T$) tends to zero at the lower limit. This phenomenon is consistent with the QCT data. This lower limit of the average vibrational energy removed in a dissociation reaction is often not represented in other models [22], [70], [71].

Due to the preferential dissociation of molecules from the upper vibrational level, the average vibrational energy removed in a dissociation reaction is much higher than the average vibrational energy. Evident in Fig. 3.4, the average vibrational energy given by the *Simple Harmonic Oscillator* model ($E_{v,SHO}$) for a dissociating molecule is much lower than the energy removed in a dissociation, except near the low vibrational limit. The non-preferential form with $E_v^{rem} = E_v$ is popular in CFD and is often used with other vibration-dissociation coupling models. Despite the inadequacy of the non-preferential form in representing the accurate vibrational energy removal in a dissociation reaction, it is commonly used in CFD because the non-preferential form is numerically robust compared to the preferential form, as the difference between the average vibrational energy and the preferential form of energy removed in dissociation is quite large. Indeed, Park's two-temperature model with a preferential form with $E_v^{rem} = 0.3D$ causes numerical instability [40] and often the non-preferential form is used. Also, the QCT data suggest that it is not accurate representation of the energy removed during dissociation. The MF-CFD model accurately represents the mean energy removed in a dissociation reaction.

3.2.2 Stanford shock tube experiment

Recent experiments at Stanford University shock tube facility utilized pulsed UV laser absorption diagnostic to measure different nonequilibrium parameters, such as the mean vibrational energy lost in dissociation and nonequilibrium dissociation rates. The results from the experiment containing varying concentration of oxygen in argon are given in Ref. [72], [73].

The experimental measurements of vibrational temperature were inferred from the absorbance ratio of the UV laser from a reflected shock in a shock tube at various operating conditions. The different aspects of nonequilibrium flow that influences the vibrational energy distribution such as the relaxation rate, oxygen concentration, translational-rotational temperature, instantaneous vibrational energy, etc. were determined to isolate the mean vibrational energy lost in dissociation from the (mean) vibrational energy conservation equation. The modified Marrone-Treanor (MMT) theory [74] was then used to isolate the nonequilibrium factor for the measured vibrational temperature and its corresponding translational temperature. The MMT is a variation of the Marrone-Treanor (MT) vibration-dissociation coupling model that uses QCT to approximate the free parameter in the MT model. The translational temperature variation in the experiment was determined using the shock jump conditions and applying the energy conservation equation with measured pressure variation.

The degree of nonequilibrium for various measured vibrational temperature and its corresponding translational-rotational temperature from experiment in Ref. [73] (Table VII) is shown in Fig. 3.5a. The measurements were made at various experimental conditions and at different stages of reflected shock, hence the data points are scattered. Since the vibrational temperatures were inferred directly from the experiment, the average vibrational energy



Figure 3.5. (a) Degree of nonequilibrium corresponding to measured vibrational temperature and comparison of MF-CFD prediction of (b) mean vibrational energy lost in dissociation and (c) nonequilibrium factor with experiment in Ref. [73].

of the molecules (E_v) were determined using various models such as the simple-harmonicoscillator, anharmonic-oscillator, NASA polynomials, etc. Here, the data obtained using the anharmonic-oscillator model in Ref. [73] are presented. The degree of nonequilibrium from various experimental conditions (different concentration of oxygen in argon) suggests that the flow is in strong nonequilibrium $(T/T_v > 1)$ at higher temperatures and is in nearequilibrium $T/T_v \approx 1$) at low temperatures, see Fig. 3.5a.

The mean vibrational energy lost in dissociation inferred from the experiment in Ref. [73] is shown in Fig 3.5b. The experimental data also have error bars in the temperature coordinate system but it is not shown in Fig 3.5b because the error magnitudes were relatively small. The experimental measurement suggests that the mean vibrational energy lost in dissociation in near-equilibrium at low temperatures in oxygen dissociation is about 70% of the dissociation energy (D). It is in contrast to the prediction made by the QCT calculations, see Fig. 3.4 (O₂ + O₂ collision), that predicts the mean energy lost to be about 80-90% of the dissociation energy. The near-equilibrium conditions in the above experiment conditions were obtained with 100% O_2 , where dissociation occurs mostly through $O_2 + O_2$ collisions. The MF-CFD model assumes that the mean vibrational energy lost in dissociation at higher vibrational level \hat{D} to be equal to the dissociation energy i.e. $\hat{D} \approx D$. Despite including the contribution of the translational energy at high vibrational level in the MF-CFD model with $\hat{D} \approx D - T$, the mean vibrational energy lost is overpredicted in the MF-CFD model, see Fig 3.5b. The lines in Fig 3.5b are a polynomial fit of the scattered data and are fitted for comparisons only and do not represent the variation of E_v^{rem} with the translational-rotational temperatures alone. At high temperatures, the MF-CFD model predictions approach the experimental predictions. It indicates the MF-CFD prediction of mean energy lost in dissociation in strong nonequilibrium is properly represented in the model. Overall, the comparison suggests that a better estimation of the mean vibrational energy lost in dissociation from higher vibrational level in the MF-CFD model could substantially improve the MF-CFD model compared to the experiments in Ref. [73].

The mean vibrational energy lost in dissociation in the MF-CFD model depends on the collision pairs. It is due to the α parameter in the MF-CFD rates that takes account of the atomic masses of collision pairs. The MF-CFD model suggests that the energy lost in

dissociation through $O_2 + Ar$ is lower compared to the $O_2 + O_2$ collisions. The experiment in Ref. [73] utilizes argon to obtain high temperature conditions where the collision between the O_2 and Ar is dominant at low oxygen concentration. In such conditions, due to the differences in atomic masses between the colliding pair, we expect significant differences in the amount of energy transfer during collisions— $O_2 + O_2$ vs. $O_2 + Ar$, that ultimately affects the mean vibrational energy lost in dissociation. However, this effect is not captured while inferring the mean vibrational energy lost in dissociation in Ref. [73]. Indeed, one can see that for a similar T/T_v obtained through varying concentration of oxygen, the mean energy lost in dissociation were predicted to be almost similar, Fig. 3.5b. In contrast, the MF-CFD model predictions are dependent on the collision pairs.

Comparison of the nonequilibrium factors $\mathcal{Z} = k(T, T_v)/k(T)$ inferred in Ref. [73] with the MF-CFD model are shown in Fig. 3.5c. The MF-CFD model underpredicts nonequilibrium factors at high temperatures. However, the MF-CFD predictions are very close to the experimental uncertainties reported in Ref. [73]. The inference of the nonequilibrium factors through experiments are strongly dependent in the deduction of the mean vibrational energy lost in dissociation. The mean vibrational energy lost in dissociation in the experiment was determined irrespective of the collision pairs and it could result in additional uncertainty in the experiments that is not reported in the experimental data shown in Fig. 3.5c. MF-CFD model suggests that the mean vibrational energy lost in dissociation through the O₂ + Ar collisions is lower compared to O₂ + O₂ collisions, see Fig. 3.5b. In reality, the mean vibrational energy lost in dissociation from various reaction pairs. An account of this phenomenon could result in prediction of lower E_v^{rem} (as suggested by the MF-CFD model) which ultimately results in prediction of lower dissociation rates, hence lower \mathcal{Z} .

3.3 MF-CFD: Rate Expressions and Parameters

In this section, a summary of all the rate expressions is presented in a form that is applicable for modeling dissociation reactions in CFD. As mentioned before, the MF model represents the multi-temperature dissociation rates as the sum of the contribution from low vibrational level and high vibrational level. Thus, the multi-temperature dissociation rate in nonequilibrium is given as:

$$k_f^{MF-CFD}(T, T_v) = k_l + k_h,$$
 (3.35)

and

$$k_{l} = AT^{n} \times L \exp\left(-\frac{D}{T_{a}} + \Delta D\left(\frac{1}{T_{a}} - \frac{1}{T}\right)\right) [\text{Eq. (3.9a, 3.31a)}],$$

$$k_{h} = AT^{n} \times (1 - L) \frac{1 - \exp(-\Theta_{v}/T_{v})}{1 - \exp(-\Theta_{v}/T)} \exp\left(-\frac{D}{T_{v}}\right) [\text{Eq. (3.12, 3.32)}].$$

Some of the parameters associated with the model are given below.

$$\alpha = \left(1 - \frac{2\mu_1}{m} \frac{M}{m+M}\right)^2$$
 [Eq. (3.7)].

with $m \in [m_B, m_A]$ and $M \in [m_C, m_D]$ based on the optimum collision arrangement that results in min (α_i) .

The L function, approximate effective dissociation energy D^* , and the definition of the average temperature T_a are different for diatom-atom and diatom-diatom collision pairs. However, the definition of T_a and D^* for diatom-diatom collision pairs can be used as a general definition with $C_1 = 1 \& C_2 = 1$ for a diatom-atom collision since these parameters are relevant for diatom-diatom collisions only. The parameters are:

$$T_{a} = (1 - \sqrt{\alpha}) (1/C_{1} + C_{2}^{2}\sqrt{\alpha}) T + \alpha T_{v} \quad [\text{Eq. (3.26b)}],$$
$$D^{*} = D - \Delta D = D - 3b (1 - (1 - \sqrt{\alpha}) (1/C_{1} + C_{2}^{2}\sqrt{\alpha}))^{2} D, \quad b = 2 \quad [\text{Eq. (3.29b)}],$$

diatom - atom collision:

$$L = \frac{\sqrt{1-\alpha}}{\pi^{3/2}} \sqrt{\frac{D}{D^*}} \left(\frac{T}{D}\right)^{1-n} \left(1 + \frac{5(1-\alpha)T}{2D^*}\right) \left(12\pi b\alpha(1-\alpha)\frac{D}{T}\right)^{1/2} \quad [\text{Eq. (3.9b)}].$$

diatom - diatom collision:

$$L = \frac{2\left(1 - \sqrt{\alpha}\right)\left(1 + C_1 C_2^2 \sqrt{\alpha}\right)}{\pi^2 C_1^{3/2} C_2 \alpha^{1/4}} \left(\frac{D}{D^*}\right) \left(\frac{T}{D}\right)^{3/2 - n} \left(1 + \frac{7T\left(1 - \sqrt{\alpha}\right)\left(1 + C_1 C_2^2 \sqrt{\alpha}\right)^2}{2C_1 D^*}\right) \times \left(12\pi b\left(1 - \sqrt{\alpha}\right)\left(1/C_1 + C_2^2 \sqrt{\alpha}\right)\left(1 - (1 - \sqrt{\alpha})\left(1/C_1 + C_2^2 \sqrt{\alpha}\right)\right)\frac{D}{T}\right)^{1/2} \quad [\text{Eq. (3.31b)}],$$

$$C_1 = \frac{\mu \mu_1}{m^2} \frac{1}{1 - \sqrt{\alpha}} \qquad C_2 = \sqrt{\frac{1 - \sqrt{\alpha}}{\sqrt{\alpha}}} \sqrt{\frac{\mu_2}{\mu_1}} \frac{m}{M} \quad [\text{Eq. (3.15b)}].$$

As a reminder, the atomic masses m and M depend on a collision configuration that results in minimum α .

The average vibrational energy removed by a dissociation reaction, in [J/kg], is:

$$\mathbf{e}_{v}^{rem} = \frac{R_{u}}{\mathcal{M}} \frac{\alpha D^{*} (T_{v}/T_{a})^{2} k_{l} + \hat{D} k_{h}}{k_{l} + k_{h}}, \quad \hat{D} = D - T.$$
(3.36)

Where, R_u is the universal gas constant (= $8.31434 \times 10^3 [J/(kmol \cdot K)]$) and \mathcal{M} is the molar mass of the dissociating species, in [kg/kmol].

The MF-CFD parameters for several dissociation reactions in air are present in Table 3.1. The parameters were calculated using a simple C++ program: https://github.com/ adnirajan/MF-CFD-Parms.

3.4 Investigation of Nonequilibrium Flows using the MF-CFD Model

In this section, various nonequilibrium flows are investigated using the developed MF-CFD model. The developed MF-CFD model was implemented into *Fluent-NEQ*.

3.4.1 Shockwaves in reacting oxygen

A shock tube experiment by Ibraguimova et al. in Ref. [75] provides vibrational temperature in a dissociating oxygen shockwave in highly nonequilibrium conditions. This experiment is often used as a nonequilibrium chemistry verification case, see Ref. [11], [29], [30], [33], [76]. The experimental conditions used in this study are summarized in Table 3.2. The equilibrium reaction rate coefficients for the shockwave case utilized in this study are given

Reactions	М	MF Parameters		
		α	C_1	C_2
$N_2 + M \rightarrow N + N + M$	N_2	0.25	1.0	1.0
	O_2	0.2179	1.0	1.0
	NO	0.2179	0.9699	0.9662
	Ν	0.25		
	Ο	0.2179		
$O_2 + M \rightarrow O + O + M$	N_2	0.2843	1.0	1.0
	O_2	0.25	1.0	1.0
	NO	0.25	0.9679	0.9662
	Ν	0.2843		
	Ο	0.25		
$NO + M \rightarrow N + O + M$	N_2	0.2179	1.0343	1.0350
	O_2	0.1861	1.0367	1.0402
	NO	0.1861	1.0044	1.0051
	Ν	0.2179		
	Ο	0.1861		

Table 3.2. Freestream conditions of shockwave in reacting oxygen.

Mach number	Shock velocity	Pressure	Temperature
	[km/s]	[Torr]	[K]
9.3 13.4	$\begin{array}{c} 3.07 \\ 4.44 \end{array}$	$\begin{array}{c} 2.0 \\ 0.8 \end{array}$	295 295

in Table 3.3. The vibrational relaxation time for collision pairs; $O_2 + O_2$ and $O_2 + O$ were obtained using the *modified Millikan-White* parameters given in Ref. [50].

The vibrational temperature distribution behind the shockwave is shown in Fig. 3.6 for shock speed of Mach 9.3 and Mach 13.4. The peak vibrational temperature for Mach 9.3 shock by the MF-CFD model is in good agreement with the experimental peak but the vibrational temperature in the aftershock region shows deviation from the experiment. For Mach 13.4 shock, the peak vibrational temperature is underpredicted by the model. The larger deviation of peak vibrational temperature in a high-speed shock can be attributed to the simple-harmonic-oscillation (SHO) assumptions. Due to the assumptions of equal spac-


Table 3.3. Rate coefficients for the MF-CFD model for reacting shockwave.

n

D

A

Reaction pair

Figure 3.6. Vibrational temperature in reacting shockwave compared to experimental measurements.

ing of energy states as well as the present of infinite energy states in the SHO model, the contribution of high vibrational states to the vibrational energy is underrepresented. This could lead to an underprediction of vibrational energy at high temperature. The vibrationaltranslational relaxation rates could also influence the distribution of the shockwave. Especially, the relaxation rates for the $O_2 + O$ collision pair from (modified) Millikan-White correlation have a limited range of validity while compared to QCT data [77]. On the other hand, as pointed out by authors in Ref. [30], [76], high uncertainty in the experimental measurements and deduction of vibrational temperature, $\sim 20\%$, makes the comparison somewhat inconclusive. Indeed, it can be seen that the vibrational temperature distribution is well within the experimental uncertainty in both cases; Mach 9.3 and Mach 13.4.

3.4.2 High enthalpy nonequilibrium flow over a HEG cylinder

High enthalpy flow over a cylinder was experimentally studied by Karl et al. [78] in the HEG shock tunnel and the experiment is often used as a nonequilibrium flow solution verification case, see Ref. [30], [79], [80]. The experiment consists of a cylinder with a radius of 45 mm and a span of 380 mm. Considering the relatively longer spanwise dimension compared to the radius of the cylinder, the flow can be modeled as two dimensional. Here, the experiment conditions of Run-627 and Run-619 in Ref. [78] are considered that are also referred to as HEG-III and HEG-I, respectively. The flow conditions are summarized in Table 3.4.

Quantity	HEG-III	HEG-I
$H_0 [{\rm MJ/kg}]$	13.5	22.4
$U_{\infty} [\mathrm{m/s}]$	4776	5956
$ ho_{\infty} \; [{ m kg/m^3}]$	3.26E-3	1.547E-3
P_{∞} [Pa]	687	476
T_{∞} [K]	694	901
Kn	2.5E-4	5.8E-4
M_{∞}	8.78	8.98
$Y_{N_2\infty}$	0.73560	0.75430
$Y_{O_{2}\infty}$	0.13400	0.00713
$Y_{NO\infty}$	0.05090	0.01026
$Y_{N\infty}$	0.0	0.0
$Y_{O\infty}$	0.07955	0.22830

Table 3.4. Test conditions for HEG cylinder.

In this case, the flow solutions were obtained utilizing the equilibrium reaction rate coefficients given by Park in Refs. [22], [50]. The vibrational relaxation rates for different species were obtained using the modified Millikan-White parameters [50] and the gas mixture transport properties were calculated using the Gupta-Yos high temperature mixing laws [45]. The wall boundary is considered to be a no-slip isothermal wall with super-catalytic (SC) cold wall conditions ($T_w = 300$ K) such that the species at the wall have a composition of $Y_{N_2} = 0.7624 \& Y_{O_2} = 0.2376$. Also, a full accommodation of vibrational temperature at the wall boundaries i.e. $T_v = T_w$ was considered.

3.4.2.1 HEG-III (Run-627) test conditions



Figure 3.7. Surface heat flux across the cylinder in HEG-III conditions.

The heat flux across the cylinder in HEG-III conditions is shown in Fig. 3.7. The stagnation point on the cylinder corresponds to the angular coordinate at $\Phi = 0$ deg. The super-catalytic boundary overpredicts the heat flux across the cylinder. The super-catalytic wall somewhat overestimates the surface catalysis that can result in the overprediction of heat flux at the surfaces. Here, the heat flux obtained with a non-catalytic boundary is also presented that is referred to as NC in Fig. 3.7 and 3.9a. The non-catalytic boundary shows the underprediction of heat flux throughout the cylinder. Judging from these two heat flux limits; super-catalytic and non-catalytic, a fully (or partial) catalytic wall might give a better agreement with the experiment. The results suggest that a proper representation of surface catalysis is important in this case for an accurate heat flux prediction. This is consistent with the observations made in Ref. [79]. On the other hand, the preferential form of the MF-CFD model overestimates the energy removed in a dissociation (or gained in recombination) reaction at low temperature. This could result in a higher vibrational temperature in the recombination dominant region (or boundary layer) which ultimately could overpredict the heat flux at a catalytic surface.



Figure 3.8. Heat flux across the cylinder using various transport models in HEG-III conditions.

The heat flux across the cylinder suggested that surface catalysis plays an important role in the heat flux predictions. In addition to the surface catalysis, the influence of various transport models that are generally used in a nonequilibrium flow solution is also considered here. Figure 3.8 presents the heat flux across the cylinder with the *Gupta-Yos* mixing laws and the *Wilke's* [46] semi-empirical mixing laws. Here, the species viscosity and thermal conductivity in Wilke's mixing laws were calculated using the *Hirschfelder* [44] model with *Lennard-Jones* collision cross-sections. Although the Gupta-Yos mixing laws are more accurate among the two transport models [45], [47], it can be seen that the heat flux with Wilke's mixing law shows better agreement with the experimental data across the cylinder. As mentioned before, this experiment is often used as a CFD nonequilibrium verification case and based on our results, the heat flux shows high sensitivity to the surface catalysis as well as the choice of transport models. So, one needs to apply caution while interpreting the results. Perhaps, a sensitivity study of various thermo-chemical models to the heat flux prediction, in this case, will be more helpful and requires a separate study.

The surface pressure across the cylinder shows good agreement with the experiment, as seen in Fig. 3.9a. The surface catalysis does not indicate any influence on the surface pressure. Although not shown here, the surface pressure was insensitive to the choice of various transport models.

The atomic nitrogen (N) mass fraction distribution along the cylinder is shown in Fig. 3.9b. The distribution of mass fraction indicates the recombination seems to be dominant close to the cylinder wall in a very thin layer.



Figure 3.9. (a) Surface pressure and (b) atomic nitrogen (N) mass fraction variation across the cylinder in HEG-III conditions.

3.4.2.2 HEG-I (Run-619) test conditions

The HEG-I flow has a higher total enthalpy than the HEG-III, see Table 3.4. The surface heat flux across the cylinder is shown in Fig. 3.10a and it shows that the heat flux is

slightly overpredicted by the MF-CFD model compared to experiment, similar to in HEG-I conditions. As mentioned above, the super-catalytic boundary overpredicts the heat flux as it assumes maximum entropy at the surface due to equilibrium assumptions. It seems that the surface catalysis significantly affects the heat flux variation in both HEG conditions. It makes these verification cases challenging because an accurate modeling of the surface catalysis is itself very challenging. A Hertz-Knudsen relation based model is often used to model surface catalysis, see Ref. [79], [81]–[83]. Current implementation in Fluent-NEQ only models non-catalytic and super-catalytic walls.

The surface pressure across the the cylinder is shown in Fig. 3.10b and the MF-CFD model shows a very good agreement with the experiment. The mass fraction for various chemical species and the temperature along the stagnation line in HEG-I conditions are shown in Fig 3.11a & 3.11b, respectively. The mass fraction variation shows a strong oxygen dissociation behind the shockwave. Also, the flow is in fairly high vibrational nonequilibrium $(T/T_v \approx 1.5)$ behind the shockwave, see Fig. 3.11b.



Figure 3.10. (a) Heat flux and (b) surface pressure variation across the cylinder in HEG-I conditions.



Figure 3.11. (a) Mass fraction and (b) temperature variation along the stagnation line in HEG-I conditions.

3.4.3 Shock standoff distance in a cone

Another interesting aspect of the nonequilibrium flow is the shock standoff distance. The shock standoff distance is affected by the thermochemical process and it becomes important to understand whether a thermochemical model can accurately predict this aspect of nonequilibrium flow. Furthermore, it gives an insight into whether a model can accurately predict a flow with a variety of geometrical complexities.

Various nonequilibrium flow conditions were experimentally investigated by Leyva in Ref. [84] over cones with varying diameter and cone angle. Here, the experimental conditions of dissociating nonequilibrium nitrogen flow over a cone with a 2 cm diameter and 70° cone angle is selected to investigate the shock standoff distance prediction in the MF-CFD model. The freestream conditions are given in Table 3.5 that corresponds to the N₂-3 conditions in Ref. [84]. The cone body is assumed to be non-catalytic isothermal wall with a temperature of 300 K.

The temperature variation along the axis of the cone is shown in Fig. 3.12a for the MF-CFD model and Park's two-temperature model. The peak translational-rotational and

$H_0 [{ m MJ/kg}]$	16.3
$U_{\infty} [\mathrm{m/s}]$	4970
P_{∞} [Pa]	8.91E-3
T_{∞} [K]	1700
$T_{v,\infty}$ [K]	3500
M_{∞}	5.54
$Y_{N_2\infty}$	0.964

Table 3.5. Test conditions for a 2 cm cone with 70° cone angle.

peak vibrational temperatures in both models are about the same. However, the shock standoff distance in the MF-CFD model is slightly larger compared to the Park model. The temperature variation along the axis in the two models suggests that Park's model reaches equilibrium before the MF-CFD model. It is probably due to the non-preferential form of vibration-dissociation coupling in the MF-CFD model. The non-preferential vibrationdissociation coupling predicts greater loss of vibrational energy to translational-rotational energy mode in a dissociation reaction compared to the preferential form and leads to stronger nonequilibrium.



Figure 3.12. (a) Temperature variation along the axis of the cone and (b) comparison of shock standoff distance with experiment.

The comparison of the shock standoff distance in the MF-CFD with the experimental measurements (from Ref. [84]) is shown in Fig. 3.12b, where the standoff distance is normalized by the cube diameter. The experimental data in the Fig. 3.12b is a curve fit (cubic fit) of the experimental measurements at various cone angles. The shock standoff distance in the MF-CFD and Park models is consistent with the experimental curve fit and it can be seen that the MF-CFD model is closer to the experiment compared to the Park model. However, the differences in the shock standoff distance between the models are very low. The Fig. 3.12b also shows the results from a high fidelity DSMC solution by the authors in Ref. [30]. The MF-CFD shock standoff distance is closer to the DSMC solution.

The atomic nitrogen mass fraction variation across the cone is shown in Fig. 3.13. Comparing the atomic mass fraction variation between the MF-CFD model and Park's twotemperature model, it can be seen that the atomic nitrogen concentration is slightly higher in the solution with Park's model. For a flow with a low degree of nonequilibrium $(T/T_v \approx 1)$, Park's model gives a solution closer to equilibrium and overestimates the dissociation. However, the differences in atomic nitrogen concentration are fairly low. Although the shock standoff distance was slightly different in the two models, the difference is minimal compared to the scale of the cone, see Fig. 3.13.



Figure 3.13. Atomic nitrogen (N) mass fraction variation across a cone with 2 cm diameter and 70° cone angle.

4. REENTRY AEROTHERMODYNAMICS OF ADE CUBESAT

Space debris is a significant threat to future space missions. Ever since the launch of the first satellite, Sputnik on the 4th of October 1957, there has been a rapid increase in traffic in the lower earth's atmosphere. As of 2021, there are about 15,000 orbiting objects in the low earth orbit (LEO) [85]. The LEO represents the orbit that is below 2,000 km of apogee height. Recently, small size satellites such as CubeSat have gain popularity deservedly due to their affordability and size. Due to the smaller size of the CubeSat, it is usually deployed and operated at a very low earth orbit (VLEO). The VLEO consists of orbits lower than 450 km in altitude. These orbits are inevitably going to be more crowded in the coming future.

Atmospheric drag will deorbit a spacecraft that will eventually lead to disintegration during its reentry. However, this is a slow process and could take more than the 25 years postmission maximum orbit lifetime mandated by the Inter-Agency Space Debris Coordination Committee (IADC) [86]. For example, an orbiting object above the 700 km perigee altitude could remain in orbit for hundreds of years. It is desirable to have an active deorbiting process to limit the lifespan of orbiting objects.

An active deorbiting of a CubeSat (post-mission) for reentry burnout can be achieved by using thrusters. Unfortunately, it is difficult to predict whether the thrusters will operate reliably towards the end of the CubeSat mission time. An alternative approach for reliable deorbiting is to use deployable drag devices such as a dragsail [87]. The large frontal area of a dragsail will considerably increase the drag of a CubeSat and result in an accelerated (passive) deorbiting. The deorbiting CubeSat disintegrates during its reentry due to the elevated aerothermal load experienced by the CubeSat. An accurate prediction of reentry trajectory of a deorbiting CubeSat is paramount to ensuring a safe disposal of the Cube-Sat. The uncertainty in reentry corridor could increase threats to air traffic as well as the ground habitat. However, determining the accurate trajectory of a CubeSat from start of the deorbiting period to the reentry burnout is extremely challenging. Atmospheric conditions change rapidly during various stages of the deorbiting and reentry period which results in the flow changing from free-molecular to the continuum regimes. Usually, a mission planning tool, such as the General Mission Analysis Tool (GMAT), is used to predict the mission path of a CubeSat at various stages of its mission. Such mission planning utilizes the drag (coefficient) on a CubeSat to predict the flight path and the prediction of drag requires an additional effort. For a free-molecular flow, we can predict the aeroload on any spacecraft analytically. However, as a spacecraft transitions to the rarefied and continuum regimes, the aeroload predictions can only be done using numerical methods because the fluid governing equations such as the Boltzmann equation, does not form an analytical solution.

Direct simulation Monte Carlo (DSMC) methods are very popular in solving rarefied flows. The DSMC solves the Boltzmann equation numerically using the Monte Carlo simulations and is valid for wide range of flow rarefaction. It is also extremely popular among researchers to investigate reentry spacecraft with a high degree of flow rarefaction, see for example Ref. [88]–[90]. Although the DSMC methods accurately represent the continuum or near-continuum flows, the methods become computationally prohibitive as the Knudsen number (Kn) decreases.

On the other hand, the Navier-Stokes-Fourier (NSF) based continuum methods offer superior computational cost savings, compared to the DSMC, but the continuum methods are valid for continuum flows only, usually for Kn < 0.01. However, the NSF based methods with a slip boundary representing the gas-surface interaction in rarefied conditions can give reasonable solutions for flows with slight rarefaction, up to the Kn ≈ 0.1 . A detailed investigation of high speed flows at various degrees of rarefaction over a cylinder using continuum methods with different slip models is given in Ref. [91]. Another study in Ref. [64] investigated slip boundary for high speed air flows over various shapes such as a cone and a hollow cylinder flare.

As mentioned before, an accurate prediction of reentry trajectory of a deorbiting CubeSat requires resolving the aerothermal load at various altitudes. Using the DSMC simulations throughout the trajectory to estimate the aerothermal load on a CubeSat will be extremely (computationally) expensive. In such cases, the NSF based methods with slip models can offer huge computational cost saving for altitudes that corresponds in near-continuum regimes. The primary objective of this work is to investigate the aerothermal load of a deorbiting CubeSat with dragsail during its reentry, using the DSMC and NSF based methods at altitudes corresponding to near-continuum flows. This work investigated the dragsail device developed by the researchers at Purdue University known as the aerodynamic deorbit experiment (ADE) CubeSat [34], [35].

Although this work primarily focuses on the ADE configuration of CubeSat with dragsail, the findings of this work can be extended to various atmospheric reentry probes as well. The drag enhancing devices could be beneficial for a reentry probe to collect atmospheric data over a longer duration. Investigation of aerothermal load on such reentry probes is equally paramount to ensure the survival of atmospheric probes over a wide altitude range.

4.1 ADE CubeSat with Dragsail

Aerodynamic deorbit experiment (ADE) includes a CubeSat with deployable dragsail. The ADE mission planned orbit is at 185 km of perigee and 35,756 km apogee altitude. The expected lifetime of the ADE CubeSat is about 50-250 days after the dragsail deployment. The configuration of the dragsail for the ADE experiment is still active research. The study in Ref. [92] considered various deorbiting CubeSat design along with two different dragsail geometric configurations; a flat sail and a 70° square pyramid sail. The stability analysis showed that the pyramid sail is more aerodynamically stable compared to the flat sail [92].

In this study, the 1U (10 cm \times 10 cm \times 10 cm) CubeSat with pyramid dragsail configuration was used. This configuration of the ADE CubeSat consists of 4 carbon fiber-reinforced polymer (CFRP) booms each of 1 m length. The sail is made of 5 micron thick polyimide material. When the dragsail deploys, the maximum projected frontal surface area will be 1.766 m² (1.33 m \times 1.33 m). A front and a side view of the ADE experimental CubeSat is shown in Fig. 4.1 with some key dimensions.

The ADE CubeSat mission will start at an altitude of 185 km and the atmospheric drag will start the deorbiting process. The reentry trajectory for the satellite is estimated to start at 100 km altitude with a flight speed of 7.5 km/s (= V_{∞} from the satellite's frame of reference). A previous study in Ref. [89] investigated the aerothermal load of the ADE CubeSat at altitudes before its reentry and at the beginning of the reentry using the DSMC methods. In this study, the conditions at the later part of the reentry at 95 km and 90 km altitudes were considered. The free-stream conditions for the two altitudes considered in



Figure 4.1. Schematic of ADE CubeSat with dragsail; (a) side view and (b) front view.

this study are shown in Table 4.1 with the Knudsen number (Kn) calculated based on the characteristic length L of 1.33 m. The Knudsen numbers suggest that the flow is in the slip regime (0.01 < Kn < 0.1) i.e. near-continuum, see Fig. 4.2.

Table 4.1. Freestream conditions for reentry of an ADE CubeSat. The conditions are based on NRLMSISE-00 Atmospheric Model (Link: https://ccmc.gsfc.nasa.gov/modelweb/models/nrlmsise00.php, visited on Feb 01, 2021).

Altitude	km	90	95
V_{∞}	m/s	7500	7500
n_{∞}	$1/m^3$	5.6463×10^{19}	2.4224×10^{19}
$\lambda_^a$	m	0.0232	0.0544
Kn	-	0.0174	0.0409

 a based on the hard-sphere assumption

Pyramid-shaped dragsail provides stability to the ADE CubeSat during its reentry. The center-of-gravity of an ADE CubeSat (1U CubeSat + dragsail) falls within the 1U CubeSat, due to its heavier weight, whereas the center-of-pressure lies behind the 1U CubeSat due to a large frontal area of the dragsail. It ultimately results in a restoring torque that stabilizes the CubeSat to a single configuration. A more detailed investigation on the stability of the ADE CubeSat is present in Ref. [89], [92]. A good analogy of this stabilizing configuration is a badminton shuttlecock that has a conical shape shuttlecock (analogous to dragsail) with a



Figure 4.2. Knudsen number variation during reentry of an ADE CubeSat.

heavier cork (similar to 1U CubeSat). An interesting investigation of the restabilizing torque in a shuttlecock is given in Ref. [93], see Fig. 4.3.



Figure 4.3. Restabilizing torque in a badminton shuttlecock [93].

As mentioned earlier, the dragsail of an ADE CubeSat is expected to be fully deployed at an altitude of 185 km and the reentry is estimated to start at 100 km. This study is interested in the altitudes of 95 and 90 km (i.e. lower part of the reentry trajectory). So, only a single stable configuration that has the freestream in the positive X-direction in Fig. 4.1 was considered, as the CubeSat will have plenty of time to equilibrate to a stable configuration— after the dragsail deployment— and before it reaches the altitudes considered in this study. Due to the symmetric body of an ADE CubeSat, only a quarter of the model simulated here to save computational time.

4.2 Computational Methods

This study utilized two different numerical methods; direct simulation Monte Carlo (DSMC) and Navier-Stokes-Fourier based continuum methods, referred to as CFD.

4.2.1 DSMC parameters

The direct simulation Monte Carlo method was developed by G. A. Bird in the early 1960s and it solves the Boltzmann equation through the Monte Carlo simulations. In DSMC, the molecules are represented by a fewer number of simulator particles along with some interaction law. The fluid domain is discretized into collision cells where the collision and transport (free flight) of particles are modeled separately. The particles are sampled to calculate macroscopic properties. Due to the stochastic nature of the method, it is required to collect macroscopic sampling over a longer duration to reduce statistical noise. Here, Sandia's SPARTA DSMC solver [94] that is based on Ref. [95] was used for DSMC simulations.

In this work, the initial grid cells in SPARTA for considered altitudes started with a size of approximately $\lambda_{\infty}/3$ and the grids were actively refined such that each cell had about 20-80 particles. A fully diffuse gas-surface interaction in the DSMC simulation was assumed with an accommodation coefficient of unity and the wall temperature of 350 K. In our DSMC simulations, the air is a reactive mixture with 11 species; N₂, O₂, NO, N, O, e, and their respective ionic counterparts. At the altitudes of 95 and 90 km (considered here), one can expect less dissociation (of molecular components in the mixture) due to the relatively low density. It ultimately affects the ionization channels that mostly have atomic species as a prime reaction component. Hence, ionization can be ignored for such high altitudes. The primary goal of this work is to assess the capability of the NSF based methods in resolving the aerothermal load on a CubeSat at such high altitudes by comparison with the DSMC. Due to this reason, the 11 species mixture in DSMC simulations are retained and comparisons with the NSF methods with a limited number of species are presented. Some additional details regarding the physical and numerical parameters used in DSMC simulations are given in Table 4.2.

e 4.4.	. Various physical and numerical parameters used in the DSWC sh			
	Domain size	$2.6~\mathrm{m}\times2~\mathrm{m}\times2~\mathrm{m}$		
	Scattering law	Variable soft sphere (VSS) $[95]$		
	Reaction model	Total collision energy (TCE)		
	Collision frequency model	No time counter (NTC)		
	Gas-surface collisions	Fully diffuse		
	Time step	$2 \times 10^{-6} \text{ s}$		

Table 4.2. Various physical and numerical parameters used in the DSMC simulations.

4.2.2 CFD parameters

A high spacecraft speed along with the rarefied conditions during a reentry result in thermochemical nonequilibrium. The thermochemical nonequilibrium significantly affects the aerothermal load of a spacecraft at such high speed and high altitudes. A CFD solver should have such nonequilibrium capabilities to accurately model flow at such conditions. Fluent-NEQ offers such unique capabilities.

This study utilized 5-species (N₂, O₂, NO, N, and O) reacting air mixture for the CFD simulations. For a rarefied flow, the vibrational energy jump at a gas-surface interface is modeled in CFD with a vibrational accommodation coefficient. However, the vibrational accommodation coefficient is orders of magnitude lower to the translational accommodation coefficient. In Ref. [64], the vibrational energy jump model was used with the vibrational accommodation coefficient (σ_v) of 10⁻³. Here, the vibrational accommodation coefficient were set at 10⁻³ for all the diatomic species in Eq. (2.45)(p. 43).

The grid used in CFD simulations contained hexahedral elements (only) with an O-grid that provides larger mesh density near the spacecraft. The grid size influence on aeroload of an ADE CubeSat was performed for 90 km altitude with no-slip boundary conditions. The flow gradients, especially near the wall boundary, are stronger at low altitudes in no-slip boundary. The final grid level had about 300,000 grid cells with a grid size length of about $\lambda_{\infty,90}/5$ in the O-grid region. Some additional details regarding the physical and numerical parameters used in CFD simulations are given in Table 4.3.

Table 4.3 . Various physical and numerical parameters used in the CFD simulations.			
Domain size	$2.6 \text{ m} \times 2 \text{ m} \times 2 \text{ m}$		
Transport model	Gupta-Yos high temperature mixing laws [45]		
Reaction model	Park's two-temperature model [22]		
Velocity slip model	Maxwell velocity slip [59]		
Temperature jump	von Smoluchowski temperature jump [61]		
Steady-state CFL number	2.0		

4.3 Flow Solution at 90 km Altitude

The aerothermal load on an ADE CubeSat at an altitude of 90 km is present in Table 4.4. It shows predictions of the drag force and the maximum heat flux experienced by the ADE CubeSat using the two different numerical methods; DSMC and CFD.

.'a <u>t</u>	ole 4.4. Aerothermal load of AL	<u>E CubeS</u>	<u>at at 90 k</u>	<u>xm altitu</u> c
			CFD	
_	Quantities	DSMC	No-slip	Slip
	Drag(N)	219.05	222.61	222.11
	Drag Coefficient	1.632	1.659	1.655
	Maximum Heat Flux (kW/m^2)	452.9	968.7	530.0

Table 4.4. Aerothermal load of ADE CubeSat at 90 km altitude.

4.3.1 Importance of a slip model in CFD at rarefied conditions

The difference in drag force between the slip and no-slip solution in CFD is only about 0.5 N. The drag in an ADE CubeSat arises mostly due to its dragsail that has a large frontal area. The (freestream) mean-free-path at 90 km altitude is about 0.02 m (Table 4.1) and the 1U CubeSat is of size 0.1 m. Thus, the 1U CubeSat experiences most of the slip due to its smaller length scale. However, the large area differences between a 1U CubeSat and its dragsail results in the overall drag being dominant by the dragsail. The contour for X-velocity across the symmetry plane and the ADE CubeSat is shown in Fig. 4.4a for both

slip and no-slip conditions. Most of the velocity slip is concentrated on the 1U CubeSat alone. The overall pressure distribution is similar between the slip and no-slip solutions, see Fig. 4.4b.



Figure 4.4. Comparison of (a) X-velocity and (b) pressure across the symmetry plane and ADE CubeSat between the slip and no-slip models in CFD at 90 km altitude.

In terms of the heat flux experienced on an ADE CubeSat, the location of the peak heat flux is on the 1U CubeSat. The translational temperature¹ contour is shown in Fig. 4.5a. It is evident that the temperature jump artificially increases the wall temperature of the 1U CubeSat. It results in a decrease in heat flux compared to the no-slip conditions. Due to this reason, the maximum heat flux is greatly affected by the temperature jump: 969 kW/m² in no-slip solution versus 530 kW/m² with the slip boundary conditions.

The temperature jump (due to the flow rarefaction) is mostly concentrated across the 1U CubeSat (similar to the velocity slip). The magnitude of the temperature jump across

¹ \uparrow In CFD, the translational and rotational energy are assumed to be in equilibrium. Hence, the translational temperature (T_t) and rotational temperature (T_r) are the same, i.e. $T_t = T_r = T_{tr} = T$.

the dragsail is fairly low. A comparison of the heat flux across the ADE CubeSat and at the symmetry plane are shown in Fig. 4.5b and Fig. 4.6 respectively, for the slip and no-slip conditions. The heat flux variations show the differences among the slip and noslip solutions are larger across the 1U CubeSat only. The heat flux distribution across the dragsail is similar between the slip and no-slip solutions with small differences near the (low pressure) recirculation region ($X_s < 0.1$ m) due to slip.

The variation of X-velocity, temperature, and pressure across the symmetry plane is similar between the slip and no-slip solutions with some differences near the 1U CubeSat at 90 km altitude, see Fig. 4.4 & 4.5. The results indicate that the slip at the gas-surface interface influences the aerothermal load on an ADE CubeSat. Especially, the peak heat flux is significantly affected due to flow rarefaction compared to the drag force.



Figure 4.5. Comparison of (a) translational-rotational temperature across the symmetry plane and ADE CubeSat and (b) heat flux across the ADE CubeSat between the slip and no-slip models in CFD at 90 km altitude.



Figure 4.6. Variation of heat flux on the ADE CubeSat across the symmetry plane in the X-direction (Fig. 4.1) between the slip and no-slip models at 90 km altitude.

4.3.2 Comparison between the CFD and DSMC solutions at 90 km altitude

The drag force on the ADE CubeSat in CFD is closer to the DSMC solution, evident in Table 4.4. A comparison of the X-velocity and pressure variation across the symmetry plane between the CFD with slip and DSMC are given in Fig. 4.7a and Fig. 4.7b, respectively.

The X-velocity across the ADE CubeSat in the symmetry plane is similar in both CFD and DSMC solutions. The shock standoff distance is slightly longer in the DSMC solution (Fig. 4.7a). A shock is more diffused at high altitude conditions such as in 90 km due to low density and the DSMC methods give a smooth variation of flow properties through the shockwave. By contrast, the CFD can not accurately resolve the shock wave for flows with extremely high Mach numbers, such as in the ADE CubeSat that has the Mach number $M \approx 27$, because the shock is treated more as a discontinuity. Regardless of the differences in the shock standoff distance, the velocity distribution in the post-shock region as well as in the wake region is accurately predicted in the CFD, with respect to the DSMC solution. The pressure distribution across the symmetric plane in Fig. 4.7b shows that the pressure variation near the 1U CubeSat is slightly different in the DSMC and the CFD solutions.



Figure 4.7. Comparison of (a) X-velocity and (b) pressure across the symmetry plane between the DSMC and CFD methods at 90 km altitude.

However, the differences are concentrated in the smaller region near the 1U CubeSat. A good agreement between the CFD and the DSMC pressure variation across the dragsail result in the drag force being closer in both methods. As mentioned earlier, a large frontal area of dragsail makes the drag force more dependent on the flow across the dragsail.

The Navier-Stokes-Fourier (NSF) continuum hypotheses are inadequate in accurately representing flows with a higher degree of flow rarefaction. It is due to the first-order assumptions in the constitutive relations and the no-slip gas-surface interaction. The slip boundary conditions address the gas-surface interaction at the rarefied conditions. In addition, to the above-mentioned phenomena that leads to a continuum breakdown, the presence of molecular components in the air at low density conditions results in strong thermodynamic nonequilibrium. The translational, rotational, and vibrational energies are in thermal relaxation for a flow with a high degree of rarefaction. The thermodynamic nonequilibrium introduces additional complexity to the flow modeling at such high altitudes. Resolving these nonequilibrium effects are inherent to the DSMC methods because of the interaction laws. In CFD, the nonequilibrium effects are modeled through the energy relaxation equations between different modes of energy. However, the translational energy and the rotational energy are usually assumed to be in equilibrium, such that the translational temperature and rotational temperature are the same, $T_t = T_r = T_{tr}$. For flows in a higher degree of rotational nonequilibrium, the assumption of rotational equilibrium could result in an inadequate representation of the temperature variation across a high-speed vehicle.

A comparison of the translational temperature and rotational temperature between the CFD and the DSMC solutions are given in Fig. 4.8a and Fig. 4.8b, respectively. The results suggest that the flow is in a strong rotational nonequilibrium. It is evident in the temperature variations along the stagnation line shown in Fig. 4.9a as well. The translational-rotational equilibrium assumption results in the temperature that is between the translational and rotational temperature in nonequilibrium. The shock standoff distance with translational-rotational equilibrium assumption will be shorter than in rotational nonequilibrium. These effects are evident in the temperature comparisons given in Fig. 4.8 and Fig. 4.9a. Despite the differences in the magnitude of temperature (that arises due to rotational nonequilibrium) between the two methods, the variation of translational temperature across the post-shock and wake are consistent in the CFD and DSMC solutions. The thermodynamic nonequilibrium is stronger in the wake region due to low pressure, as seen in the rotational temperature comparison in Fig. 4.8b.

At high altitudes, vibrational energy will be in a strong nonequilibrium as well. The translational and rotational nonequilibrium influences the vibrational temperature distribution due to the energy transfer between different energy modes. A comparison of vibrational temperature of the flow around the ADE CubeSat is shown in Fig. 4.9b between the DSMC and CFD solutions. For both methods, the vibrational temperature represents the average vibrational energy of the flow, considering all diatomic molecules present in the flow. Although the variation of vibrational temperature is similar between the two different methods, the differences in the vibrational temperature variation, especially in the wake, can be attributed to the thermodynamic nonequilibrium modeling in the two methods; rotational nonequilibrium in DSMC versus the translational-rotational equilibrium in CFD. The DSMC



Figure 4.8. Comparison of (a) translational and (b) rotational temperatures across the symmetry plane between the DSMC and CFD methods at 90 km altitude.

solution suggests stronger vibrational nonequilibrium in the wake region compared to the CFD. The vibrational relaxation rates for various molecular components are slightly different in the two methods; the DSMC solution utilizes the original Millikan-White relaxation rates [49] whereas, in CFD, the modified Millikan-White relaxation rates [50] were used with the Park's high-temperature corrections [22]. It could lead to an additional disagreement in the vibrational temperature distribution.

The heat flux distribution across the ADE CubeSat is influenced by the temperature variation across the CubeSat, primarily the temperature jump due to the flow rarefaction at the gas-surface interface. The temperature jump conditions in the CFD addresses this (important) factor of the rarefied flow. Figure 4.10a shows a comparison of the heat flux variation across the ADE CubeSat for both numerical methods. The heat flux prediction across the 1U CubeSat in the CFD solution is similar to the DSMC solution, and the location



Figure 4.9. Variation of (a) translational and rotational temperatures along the stagnation line and (b) vibrational temperature across the symmetry plane between the DSMC and CFD methods at 90 km altitude.

of the peak heat flux is consistent among the two numerical methods. The heat flux across the dragsail is fairly low, compared to the 1U CubeSat, as predicted in both numerical approaches. The overall heat flux prediction in the CFD solution is in good agreement with the DSMC solution, with slight differences towards the end of dragsail. The heat flux variation across the CubeSat in the symmetry plane in the Y-direction is shown in Fig. 4.10b. The heat flux across the symmetry plane is similar to the DSMC solution with CFD predicting slightly higher heat flux towards the edge of the CubeSat ($Y_s \approx 0.05$ m). The peak heat flux in the CFD solution is only about 80 kW/m² higher than the DSMC solution, see Table 4.4.

Another important aspect of the flow at high altitudes is the chemical reactions. Due to low density at high altitudes, such as above 90 km considered in this study, the dissociation reactions become less prominent. The relatively lower bond energy of oxygen molecules



Figure 4.10. Heat flux variation (a) across the ADE CubeSat and (b) in the 1U CubeSat along the Y-direction of the symmetric plane between the DSMC and CFD methods at 90 km altitude.

results in the atomic oxygen becoming readily available, due to oxygen dissociation, compared to the atomic nitrogen. The atomic oxygen (O) generated from the dissociation of oxygen molecules (O₂) reacts with the most prevalent nitrogen molecule (N₂) and produces nitric oxide (NO). This reaction is known as the Zeldovich exchange reaction. Figure 4.11 shows a variation of nitric oxide number density across the ADE CubeSat at 90 km altitude. The DSMC predicts a slightly higher nitric oxide concentration compared to the CFD. It is due to the differences in the chemical reaction model between the two methods. The total collision energy (TCE) model in the DSMC does not depend on the degree of vibrational nonequilibrium, unlike Park's two temperature model [22] in CFD. Park's two temperature model suppresses the dissociation reaction when the vibrational temperature is low. The flow around the ADE CubeSat is in strong vibrational nonequilibrium, see Fig. 4.9b & 4.8a. It results in a lower concentration of nitric oxide due to a deficiency in atomic oxygen. However, the NO concentration between the two methods is fairly close (same order of magnitude), probably due to a low level of dissociation at high altitudes. The development of a dissociation model depending on the vibrational nonequilibrium in the DSMC is active research, see Ref. [30], [33].



Figure 4.11. Nitric oxide (NO) concentration across the symmetric plane between the DSMC and CFD methods at 90 km altitude.

4.4 Flow Solution at 95 km Altitude

The aerothermal load on the ADE CubeSat during reentry at the altitude of 95 km is present in Table 4.5. The drag force predictions between the two numerical methods are within 4 N.

The results from the 90 km and 95 km altitudes (Table 4.4 & 4.5) suggest that the drag force in CFD is closer to the DSMC solution even for a greater degree of flow rarefaction. A comparison of the X-velocity and pressure across the symmetry plane for 95 km altitude are shown in Fig. 4.12a and Fig. 4.12b, respectively. Unlike the results for 90 km altitude, the X-

-			0 0 0
	Quantities	DSMC	CFD
	Drag (N)	96.94	100.92
	Drag Coefficient	1.696	1.765
	Maximum Heat Flux (kW/m^2)	226.5	367.2

Table 4.5. Aerothermal load of ADE CubeSat at 95 km altitude.

velocity and pressure are not in good agreement between these two numerical methods. The X-velocity in CFD shows a strong disagreement with the DSMC solution in the wake region, whereas the pressure distribution across the 1U CubeSat and dragsail also showed deviation between the two methods. However, the disagreement only leads to a minor difference in the overall drag force, about 4 N.



Figure 4.12. Comparison of (a) X-velocity and (b) pressure across the symmetry plane between the DSMC and CFD methods at 95 km altitude.

In contrast to the drag force, the peak heat flux in the CFD shows a significant difference compared to the DSMC solutions at 95 km altitude, i.e. 367 kW/m^2 in CFD versus 227

 kW/m^2 in DSMC. The freestream mean-free-path at 95 km altitude is about 0.054 m. The smaller sized 1U CubeSat will experience extreme effects of flow rarefaction. In such a high degree of flow rarefaction, the CFD methods are inadequate in accurately representing the flow features, even with the slip/jump models. Figure 4.13a shows the heat flux across the ADE CubeSat, and Fig. 4.13b presents the heat flux variation in 1U CubeSat in the Y-direction across the symmetry plane. The heat flux distribution on the ADE CubeSat suggests that the CFD significantly over predicts the heat flux, compared to the DSMC, of about 140 kW/m².



Figure 4.13. Heat flux variation (a) across the ADE CubeSat and (b) in the 1U CubeSat along the Y-direction of the symmetric plane between the DSMC and CFD methods at 95 km altitude.

4.5 Continuum Breakdown at High Altitudes

A large discrepancy in the CFD and DSMC in predicting the aerothermal load on an ADE CubeSat at 95 km altitude is due to a greater degree of flow rarefaction, which leads

to continuum breakdown. A continuum breakdown is difficult to determine however a local Knudsen number that depends on the gradient of macroscopic quantities is often used to characterize the continuum breakdown. For a macroscopic flow quantity with a strong gradient in parts of the flow, the variation can be over a distance comparable to the molecular scale (given by the mean-free-path). In such conditions, one can assume continuum breakdown. The continuum breakdown usually happens in shock, boundary layer, and wake due to the variation of macroscopic quantities over a short distance.

A gradient-based local Knudsen number, referred to as gradient length local (GLL) Knudsen number, is often used to characterize the continuum breakdown [95], [96]. It is defined as:

$$Kn_{GLL} = \frac{\lambda}{Q} \left| \frac{dQ}{dl} \right| \tag{4.1}$$

Where, Q is the quantity of interest such as density, pressure, velocity, etc. and the derivative is based on the direction of the maximum gradient at a location. The continuum hypothesis is assumed to break when $Kn_{GLL} > 0.05$. Pressure was used as a quantity of interest to calculate the continuum breakdown parameter in Eq. (4.1). Here, the mean-free-path is defined as [97]:

$$\lambda = \frac{2\mu}{\rho\bar{c}} = \frac{\mu}{\rho} \sqrt{\frac{\pi}{2RT}}$$
(4.2)

Figure 4.14 shows the local Knudsen number variation across the ADE CubeSat for 90 km and 95 km altitudes, obtained in CFD. As expected, the breakdown of the continuum hypothesis, $Kn_{GLL} > 0.05$, can be seen in the region of shock, boundary layer, and wake. The shock is more diffused at 95 km hence the continuum breakdown spreads over a larger region. Compared to the 90 km altitude, the 1U CubeSat experiences a larger region of continuum breakdown at 95 km. The wake region at 95 km altitude falls under the rarefied regime, with the local Knudsen number greater than 0.1. It explains the significant differences between the CFD and DSMC predictions of aerothermal load on the ADE CubeSat at 95 km altitude.

Despite both altitudes considered in this study lying within the slip regime— based on the Knudsen number calculated using the characteristic length (Table 4.1), the flow solutions for 95 km altitude in CFD show large deviation from the DSMC results. It is primarily due to the conical shaped body of an ADE CubeSat with dragsail that results in elevated slip effects near the smaller sized CubeSat. It shows that a characteristic length based Knudsen number does not provide a good estimation for validity of the continuum based methods for conical-shaped spacecrafts.



Figure 4.14. Continuum breakdown parameter: local Knudsen number Kn_{GLL} for 90 and 95 km altitudes.

The results presented here suggest that the applicability of the continuum based methods are limited to altitudes $H \leq 90$ km. The continuum breakdown restricts an accurate prediction of aerothermal load on an ADE CubeSat for higher altitudes. A smaller sized 1U CubeSat in an ADE configuration results in the 1U CubeSat experiencing a strong continuum breakdown. It ultimately affects the flow prediction capabilities of continuum based models. A more accurate slip model in CFD, such as the Gokcen general slip model [97], might improve the heat flux predictions. However, only a minor improvement can be expected due to the large degree of flow rarefaction for altitudes above 90 km. A study in Ref. [91] showed only a slight improvement in heat flux predictions (on comparison with DSMC solution) with the Gokcen model for the flow with a higher degree of rarefaction, compared to the traditional von Smoluchowski model [61].

The primary goal of this work was to access the flow prediction capabilities of continuum based methods for altitudes where DSMC methods are usually preferred. However, it should be noted that some of the nonequilibrium phenomena— such as the internal energy relaxation, dissociation reactions, transport properties— are not accurately modeled by DSMC methods. For example, the previously mentioned limitation of total collision energy model that does not represent the vibrationally favoring dissociation. In contrast, Park's two-temperature model in CFD takes account of this phenomenon albeit being of an empirical nature. On the other hand, although the variable soft sphere (VSS) or variable hard sphere (VHS) models use a viscosity index that is consistent with experimental observations, the scattering model does not necessarily resolve the mixture viscosity accurately. The development of transport models that are consistent in DSMC and CFD is an active area of research, see Ref. [98]. Assessing the consistency of the DSMC and CFD transport models in representing complex nonequilibrium flows in detail requires a different study and is beyond the scope of this work.

The drag force and heat flux for the two altitudes considered in this study are fairly high $(drag > 100 \text{ N} \text{ and peak heat flux} > 200 \text{ kW/m}^2)$, Table 4.5 & 4.4. It will be interesting to see if an ADE CubeSat configuration can handle such a high heat flux and drag force during its reentry and reach the altitudes considered in this study without disintegration. The experimental studies, such as in Ref. [99], will provide a better insight into the structural integrity of an ADE CubeSat. The development of an ADE CubeSat is active research [89], [92], and the results presented in this work provide a valuable insight into the estimation of aerothermal load on the ADE configuration considered in this study.

4.6 Ionization at High Altitudes

A low level of dissociation in the flow at high altitudes leads to a low concentration of ionization because most ionization reaction in the air involves atomic species as a primary reactant for various ionization channels. Figure 4.15 presents NO⁺ concentration (most

prominent ionic species in the air) for two different altitudes: 90 km and 95 km, across the symmetry plane. The NO⁺ concentration is low at altitudes considered in this study. Hence, the flow can be represented accurately with just 5-species of air, as a mixture of N₂, O₂, NO, N, & O. This is probably the reason for a good agreement between the CFD and DSMC solutions (at 90 km altitude), where the CFD solutions utilized 5-species air mixture.



Figure 4.15. Ionic nitric oxide (NO⁺) concentration at 90 km and 95 km altitudes.

4.7 Computational Requirements and Cost

A prime advantage of using continuum based methods in modeling near-continuum flows is the computational cost savings. The DSMC methods become computationally prohibitive for flows that are in near-continuum.

A DSMC simulation for 90 km altitude took about 32 hours utilizing 256 cores on a typical high-performance computing (HPC) cluster with 128 CPU cores (2.0 GHz CPUs) and 256 GB of memory per node. The fluid domain had about 400 million simulator particles. The same (altitude) case in CFD simulation (with slip models) took only about 6 hours with 16

grid partitions on a typical Xenon workstation that had 40 cores (2.5 GHz CPUs) in total with 126 GB memory. The computational grid in the CFD simulations had about 300,000 grid cells. Concerning the demanding computational overhead in the DSMC methods for modeling near-continuum flows, a significant advantage in reduced computational time and reduced computational requirements can be seen with the CFD. Although the CFD methods offer a considerable advantage in computational cost-saving, one should be aware that the applicability of the continuum methods are limited to lower altitude cases only, as indicated by the results presented here.

For a higher altitude of 95 km, the DSMC simulation took about 10 hours on 128 cores (using the same HPC node as in 90 km). A significant difference in the computational cost between the 90 km and 95 km altitudes in DSMC. As the flow rarefaction increases, the DSMC methods become cost-effective. For the 95 km case, there were about 63,000 simulator particles in the fluid domain. The CFD simulation for 95 km altitude utilized the same grid and took about the same time as in 90 km altitude.

The lower altitudes carry great significance while predicting the reentry trajectory of an ADE CubeSat, primarily to ensure a predictable trajectory during its reentry. The CFD methods can be an alternative to the DSMC in calculating such trajectories because of the computational cost savings offered at low altitudes.

5. SUMMARY

Fluent-NEQ Development:

In this study, a general purpose CFD solver, *ANSYS Fluent*, was modified to include nonequilibrium models in air with 5-species reacting mixture through the use of UDFs. All the components of the flow solution affected by the nonequilibrium effects were modified using their respective UDFs.

The implemented nonequilibrium models in Fluent-NEQ were used to solve various nonequilibrium flow problems and the results were in good agreement with the experiments. The results indicate proper implementation of the nonequilibrium models in Fluent-NEQ. In addition, a comparison between the equilibrium and nonequilibrium solutions demonstrated that it is essential to include the nonequilibrium phenomenon while modeling high speed nonequilibrium flows, especially for accurate surface heat flux prediction.

A good agreement of the various flow solutions obtained in Fluent-NEQ with the available experimental data suggests that a commercial equilibrium CFD solver can be successfully modified to solve nonequilibrium flow problems in air. Overall, it can be concluded that the process of modifying a commercial solver to solve nonequilibrium flow problems can offer a huge advantage in saving time and effort in the development of a nonequilibrium solver. At present, ANSYS Fluent does not allow overloading of the Riemann solver through UDFs. If such capabilities are available in the future, it will further extend its application as a prominent research tool. The author believe the developed solver presented here establishes the possibilities of simulating more complex fluid-thermal and electromagnetic coupled problems in thermochemical nonequilibrium since most of the thermal and electromagnetic models are already available in the ANSYS Fluent package.

MF-CFD Development:

This work also presents the development of a general form of the Macheret-Fridman classical impulsive dissociation model referred to as MF-CFD. The MF-CFD model was derived by revisiting the classical impulsive theory for a heteronuclear molecule dissociating at the impulsive limit. The nonequilibrium dissociation rates from the MF-CFD model compared well with the QCT data for the considered reaction pairs. Some improvements to the prediction of average vibrational energy removed in a dissociation reaction by the MF-CFD model are proposed here based on the comparison with available QCT data. The developed MF-CFD model was used to investigate various nonequilibrium flow problems and the results were consistent with the available experimental data.

Overall, the results indicate that the MF-CFD model accurately represents several aspects of a dissociation reaction in nonequilibrium. The model has shown the potential of becoming a standard vibration-dissociation coupling model in CFD.

ADE CubeSat Reentry:

The reentry aerothermodynamics of an ADE CubeSat was studied numerically for the altitudes in near-continuum regime using the DSMC methods and continuum based CFD methods with slip boundary models. The Navier-Stokes-Fourier based continuum methods with the slip models, representing the gas-surface interaction in the rarefied conditions, were used to model the near-continuum flows. The flow slip/jump significantly influences the heat flux. The peak heat flux in the CFD with the slip models was closer to the DSMC solutions than with the no-slip model. The results indicate that the no-slip models can not accurately predict the aerothermal load of an ADE CubeSat at the altitudes considered in this study.

The drag and heat flux predictions from the CFD solutions were in good agreement with the DSMC solution for the altitude of 90 km. Various flow properties, such as the X-velocity and pressure, were accurately represented in the CFD simulations. The DSMC solutions indicated strong rotational nonequilibrium in the flow at high altitudes. Regardless of the CFD models assuming a translational-rotational equilibrium, the heat flux on the ADE CubeSat at the 90 km altitudes were in good agreement with the DSMC solutions.

The flow at 95 km altitude has a higher degree of rarefaction. The continuum breakdown at such a high altitude significantly affected the flow prediction capability of the continuum based methods. The flow solutions by the CFD methods were not in good agreement with the DSMC solutions at 95 km altitude. Hence, the applicability of the continuum based methods is limited to the altitudes that are closer to 90 km.
It is essential to accurately predict the aerothermal load on a CubeSat at low altitudes to estimate the reentry corridor for safe disposal of the CubeSat during its reentry burnout. The computational requirements between the two numerical methods (considered here) showed that the continuum based methods offer significant (computational) cost savings for modeling the near-continuum flows, especially at low altitudes, less than 90 km. The continuum based methods can be complementary to the DSMC methods in calculating reentry trajectory over the wide range of altitudes.

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A. PARTIALLY IONIZED FLOW IN FLUENT-NEQ

A high temperature behind a strong shock can initiate ionization in the flow. The primary channel for ionization in, the air at high temperature, is the associative ionization channel that involves atomic oxygen and atomic nitrogen, $N + O \longrightarrow NO^+ + e^-$. The atomic species become readily available due to the dissociation of the constitutive molecular components at high temperatures and initiate the ionization reaction. The relatively smaller atomic mass of the free electron results in the inefficient energy exchange between the electrons and heavy particles. Hence, there will be an electron energy relaxation in the flow and this requires an additional relaxation equation that models the energy relaxation between the free electrons and heavy particles in the flow.

The electron translational energy is usually in strong thermodynamic nonequilibrium due to inefficient energy transfer during a collision. Usually, the electron translational energy relaxation is the slowest process in the thermodynamic nonequilibrium compared to rotational and vibrational relaxation. However, it is a reasonable assumption to assume the electron translational energy to be in equilibrium to the vibrational energy as the two relaxation processes are the slowest in the thermochemical nonequilibrium, i.e. $T_v = T_e = T_{ve}$. This approach is still the two temperature modeling of thermochemical nonequilibrium but the two temperatures are defined as; translational-rotational (T_{tr}) and vibrational-electrontranslational (T_{ve}) temperatures. It is also common to model the electron-translational energy separately in a 3-temperature approach, see Ref. [100], [101]. However, the results from 2-temperature and 3-temperature models are often very similar for a variety of flows, see for example Ref. [101].

Modeling of the partially ionized flow with electron-translational nonequilibrium in Fluent-NEQ requires solving electron-translational energy relaxation equation addition to vibrational energy relaxation equations, that are given in Chapter 2 Sec. 2.2 (p. 23). Additionally, the translational-rotational relaxation equation is solved for the heavy particles with appropriate energy transfer source terms. The current implementation of the Fluent-NEQ models the partially ionized nonequilibrium flow with 7 species reacting air mixture; $N_2, O_2, NO, NO^+, N, O, \& e^-$, using the two-temperature approach. The characteristic temperature associated with the electronic excitation states (levels) of the heavy particles in the air is widely spread out. Hence, there are only a few electronic states that lie below the dissociation limit for most molecules. Due to this reason, the electronic excitation is ignored in the Fluent-NEQ. The current implementation of the Fluent-NEQ assumes that the energy contained in the electronic modes are negligible compared to other modes, similar to in Ref. [43]. However, it might become important to include a few electronic states to accurately model the influence of electronic excitation to chemical reactions.

The electron-translational relaxation equation is given as:

$$\frac{\partial \rho_{\rm e} e_{\rm e}}{\partial t} + \frac{\partial}{\partial x_{\rm i}} [\rho_{\rm e} e_{\rm e} u_{\rm i}] - \frac{\partial}{\partial x_{\rm i}} [q_{\rm e,i} - e_{\rm e} J_{\rm e,i}] = S_{\rm e}$$
(A.1)

where,

$$\mathbf{e}_{\mathbf{e}} = C_{v,\mathbf{e}}T_{\mathbf{e}} + u_{\mathbf{i}}u_{\mathbf{i}}/2,\tag{A.2}$$

$$q_{\rm e,i} = \eta_{\rm e} \partial_{\rm i} T_{\rm e} \tag{A.3}$$

$$S_{\rm e} = S_{\rm epg} + S_{tr-\rm e} + S_{react,\rm e} \tag{A.4}$$

 e_e is the electron-translational energy per unit mass of electrons, $C_{v,e}$ is the specific heat at constant volume for electrons, and S_e is the source term representing various energy transfer mechanisms. S_{epg} is the approximation of the work done by the electric field induced by the electron pressure gradient and is given as (Ref. [102]):

$$S_{\rm epg} = -P_{\rm e} \nabla \cdot \vec{u} \tag{A.5}$$

where, $P_{\rm e}$ is the electron pressure.

The energy transfer between the free electron and the heavy particles (elastic collisions) is represented by S_{tr-e} and is given as:

$$S_{tr-e} = 3R_u \rho_e (T_{tr} - T_e) \sqrt{\frac{8R_u T_e}{\pi M_{w,e}}} \sum_{s \neq e} \frac{\rho_s N_A}{M_{w,s}^2} \sigma_{es}$$
(A.6)

where σ_{es} is the collision cross-sections between the electron and the heavy particles. The parameters for electrons-ions collision cross-sections are obtained from Ref. [102]. The Coulomb collision is often used to determine the collision cross-sections between the electron and ions, see Ref. [58], [100].

The rate of change of electron translational energy due to chemical reaction (associative ionization or dissociative recombination in 7-species air mixture) is represented by $S_{react,e}$ and is given as:

$$S_{react,e} = w_e e_e^{hpc} \tag{A.7}$$

where $w_{\rm e}$ is the rate of gain/loss of electrons in chemical reactions and $e_{\rm e}^{hpc}$ is the average energy of the newly formed electron from heavy particle collisions.

$$\mathbf{e}_{\mathbf{e}}^{hpc} = \frac{3}{2} \frac{R_u}{M_{w,\mathbf{e}}} T_{\mathbf{e}} \tag{A.8}$$

The electron translational heat flux contribution can be often ignored because of the low thermal conductivity, such that $q_e = 0$ (Ref. [43]). Here in Fluent-NEQ, the q_e is approximated using Eucken's relation such that: $q_{e,i} = \frac{5}{2}Y_e\mu_e\partial_i e_e$. It reduces the electrontranslational energy relaxation equation to the user-defined-scalar transport equation in *ANSYS Fluent*, see Eq. (2.33) (p.31). Additionally, the transport properties in Fluent-NEQ for partially ionized flow is modeled using the Gupta-Yos high temperature mixing laws [45] utilizing viscosity collision integrals from Ref. [103] for electron-ions collisions.

A.1 Fluent-NEQ Implementation

ANSYS Fluent only allows the overloading of the C_p for species and mixture. The translational-rotational energy relaxation equation in Fluent calculates the electron translational energy as a function of translational-rotational temperature (T_{tr}) . For the flows with electron-translational nonequilibrium, the electron translational energy is represented by the vibrational-electron-translational temperature (T_{ve}) in a two-temperature approach. Hence, the correction terms were introduced to the solver as source terms to cancel the contribution of the free electrons from the translational-rotational energy equation and reduce it to a heavy particle translational-rotational energy relaxation equation.

The mixture density in a partially ionized flow with thermodynamic nonequilibrium is given as:

$$\rho = \frac{P}{R_u \sum_{s \neq e} Y_s / M_{w,s} T + Y_e / M_{w,e} T_e}$$
(A.9)

The compressible solver (density-based solver) in the ANSYS Fluent package does not allow the overloading of mixture density. The mixture density is calculated as a function of translational-rotational temperature, i.e. $\rho(T)$. It has minimal impact on flows with a small degree of ionization because the electron pressure, $P_{\rm e} = \rho R u Y_{\rm e}/M_{w,{\rm e}}T_{\rm e}$, is very low compared to the partial pressure of heavy particles. A full implication of this limitation needs to be studied and is left as future work. Hence, the 7-species implementation in the Fluent-NEQ is presented in the Appendix. Maybe the future versions of Fluent will allow overloading of the mixture density.

A.2 Nonequilibrium Flow over the Ram-C II Spacecraft

The implementation of 7-species nonequilibrium flow in Fluent-NEQ is used to model the high speed flow over the Radio Attenuation Measurement (RAM) experiment spacecraft. The experiment was carried out to study the communication blackout during reentry. It is very popular among researchers to verify various nonequilibrium models, see for example Ref. [8], [43], [100], [101]. Out of several flight conditions, the Ram-C II flight test conditions corresponding to the H = 61 km altitude in the reentry trajectory are selected here for comparisons. Ram-C II is conically shaped with a blunt nose. The nose radius is 0.1524 m and the cone angle is 9 deg. The length of the vehicle is 1.3 m. The freestream conditions for 61 km altitude in the Ram-C II experiment are given in Table. A.1.

The reaction sets given by Park in Ref. [50] were used to model the flow along the Ram-C II spacecraft with the equilibrium constants given in Ref. [22]. Park's two-temperature model was used to model the dissociation reactions. The wall boundary is assumed to be non-catalytic isothermal with a wall temperature of 1000 K.

$U_{\infty} [\mathrm{m/s}]$	7650
P_{∞} [Pa]	21.2
T_{∞} [K]	243
M_{∞}	24.4
$Y_{N_2\infty}$	0.233
$Y_{O_2\infty}$	0.767

 Table A.1. Test conditions for Ram-C II spacecraft at 61 km altitude.

The free electron number density across the Ram-C II spacecraft is shown in Fig. A.1a and the maximum electron number density normal to the wall at various axial locations in the Ram-C II spacecraft is compared with the experimental measurement [104] in Fig. A.2. The distribution of free electron number density shows good agreement with the experimental measurements. The results suggest that the Fluent-NEQ can predict the free electron number density accurately in Ram-C II spacecraft at 61 km altitude.



Figure A.1. (a) Electron number density (n_e) across the body and (b) maximum electron number density normal to the surface at various axial location in the Ram-C II spacecraft at 61 km altitude.

The temperature variation along the stagnation line and the contour of vibrationalelectron-translational temperature across the Ram-C II spacecraft are shown in Fig A.2a & A.2b, respectively. The mass fractions for various species along the stagnation line (axis) species is shown in Fig. A.3.



Figure A.2. (a) Temperature variation along the stagnation line and (b) vibrational-electron-translational temperature across the body in the Ram-C II spacecraft at 61 km altitude.



Figure A.3. Mass fractions variation along the stagnation line in the Ram-C II spacecraft at 61 km altitude.

B. PHYSICAL AND CHEMICAL DATA

Table D.1. Species data.								
Species	MW, kg/kmol	$h^0, J/kg$	Θ_{vib}, K	f_{tr}				
N_2	28.0134	0.0	3.395E + 3	3 + 2				
O_2	31.9988	0.0	2.239E + 3	3 + 2				
NO	30.0061	3.0418E + 6	2.817E + 3	3 + 2				
Ν	14.0067	3.3747E + 7	-	3 + 0				
0	15.9994	$1.5574E{+}7$	-	3 + 0				

Table B.1. Species data.

Interaction	$A_{(1,1)}$	${ m B}_{(1,1)}$	$C_{(1,1)}$	$D_{(1,1)}$
N ₂ - N ₂	-6.0614558E-03	1.2689102E-01	-1.0616948E+00	8.0955466E + 02
N ₂ - O ₂	-3.7959091E-03	9.5708295 E-02	-1.0070611E + 00	$8.9392313E{+}02$
N_2 - NO	-1.9295666E-03	2.7995735 E-02	-3.1588514E -01	1.2880734E + 02
N ₂ - N	-1.0796249E-02	2.2656509E-01	-1.7910602E+00	4.0455218E + 03
N ₂ - O	-2.7244269E-03	6.9587171E-02	-7.9538667E-01	4.0673730E + 02
O ₂ - O ₂	-8.0682650E-04	1.6602480E-02	-3.1472774E-01	1.4116458E + 02
O_2 - NO	-6.4433840E-04	8.5378580E-03	-2.3225102E-01	1.1371608E + 02
O ₂ - N	-1.1453028E-03	1.2654140E-02	-2.2435218E-01	7.7201588E + 01
O ₂ - O	-4.8405803E-03	1.0297688E-01	-9.6876576E-01	6.1629812E + 02
NO - NO	-0.0000000E+00	-1.1056066E-02	-5.9216250E-02	7.2542367E + 01
NO - N	-1.5770918E-03	1.9578381E-02	-2.7873624E-01	$9.9547944E{+}01$
NO - O	-1.0885815E-03	1.1883688E-02	-2.1844909E-01	$7.5512560E{+}01$
N - N	-9.6083779E-03	2.0938971E-01	-1.7386904E+00	3.3587983E + 03
N - O	-7.8147689E-03	1.6792705E-01	-1.4308628E + 00	$1.6628859E{+}03$
O - O	-6.4040535E-03	1.4629949E-01	-1.3892121E+00	2.0903441E + 03

Table B.2. Parameters for collision cross-sections $\pi \Omega_{sr}^{(1,1)}$ and $\pi \Omega_{sr}^{(2,2)}$ (Å²) [45].

Interaction	$A_{(2,2)}$	$B_{(2,2)}$	$C_{(2,2)}$	$D_{(2,2)}$	
N ₂ - N ₂	-7.6303990E-03	1.6878089E-01	-1.4004234E+00	2.1427708E+03	
N ₂ - O ₂	-8.0457321E-03	1.9228905 E-01	-1.7102854E + 00	5.2213857E + 03	
N_2 - NO	-6.8237776E-03	1.4360616E-01	-1.1922240E+00	1.2433086E + 03	
N ₂ - N	-8.3493693E-03	1.7808911E-01	-1.4466155E+00	1.9324210E + 03	
N ₂ - O	-8.3110691E-03	1.9617877E-01	-1.7205427E+00	4.0812829E + 03	
O ₂ - O ₂	-6.2931612E-03	1.4624645 E-01	-1.3006927E+00	1.8066892E + 03	
O_2 - NO	-6.8508672E-03	1.5524564 E-01	-1.3479583E+00	2.0037890E + 03	
O ₂ - N	-1.0608832E-03	1.1782595 E-02	-2.1246301E-01	$8.4561598E{+}01$	
O ₂ - O	-3.7969686E-03	7.6789981 E-02	-7.3056809E-01	$3.3958171E{+}02$	
NO - NO	-7.4942466E-03	1.6626193E-01	-1.4107027E+00	2.3097604E + 03	
NO - N	-1.4719259E-03	1.8446968E-02	-2.6460411E-01	1.0911124E + 02	
NO - O	-1.0066279E-03	1.1029264 E-02	-2.0671266E-01	8.2644384E + 01	
N - N	-7.7439615E-03	1.7129007E-01	-1.4809088E+00	2.1284951E + 03	
N - O	-5.0478143E-03	1.0236186E-01	-9.0058935E-01	4.4472565E + 02	
0 - 0	-4.2451096E-03	9.6820337E-02	-9.9770795E-01	8.3320644E+02	

	Woulled Willikan- Willee S paran								
	Collision Pair	A_{sr}	B_{sr}						
-	N ₂ - N ₂	221.53	0.0290						
	N ₂ - O ₂	228.76	0.0295						
	N_2 - NO	225.30	0.0293						
	N ₂ - N	180.88	0.0262						
	N ₂ - O	72.40	0.0150						
-	O ₂ - N ₂	131.32	0.0295						
	O ₂ - O ₂	135.91	0.0300						
	O_2 - NO	133.71	0.0298						
	O ₂ - N	72.40	0.0150						
	O ₂ - O	47.70	0.0590						
-	NO - N_2	49.50	0.0420						
	NO - O_2	49.50	0.0420						
	NO - NO	49.50	0.0420						
	NO - N	49.50	0.0420						
	NO - O	49.50	0.0420						

 Table B.3.
 Modified Millikan-White's parameters [50].

	rolling Temperature T,	<i>co</i> -		T	T	T	T	T	T		T	T
ents [50].	Rate Conti T	т cf		$T^{\alpha}T_{v}^{1-\alpha}$	$T^{\alpha}T_{v}^{1-\alpha}$	$T^{\alpha}T_{v}^{1-\alpha}$	$T^{\alpha}T_v^{1-\alpha}$	$T^{\alpha}T_v^{1-\alpha}$	$T^{\alpha}T_{v}^{1-\alpha}$		T	T
rate coefficie	oefficients E.,	J/kmol		9.4000E + 8	9.4000E + 8	4.9368E + 8	4.9368E + 8	6.2856E + 8	6.2856E + 8		3.1178E+8	1.6379E+8
ns and	Rate C h	2		-1.6	-1.6	-1.5	-1.5	0.0	0.0		-1.0	0.0
nical reactio	Forward I A	$m^3/kmol \cdot s$		7.0E + 18	$3.0E{+}19$	$2.0E{+}18$	$1.0E{+}19$	$5.0E{+}12$	1.1E + 14		$6.4E{+}14$	8.4E + 09
ble B.4. Cher	Μ			N_2 , O_2 , NO	N, O	N_2 , O_2 , NO	N, O	N_2, O_2	NO, N, O			
Ta	Reactions		Dissociation	$N_2 + M \rightleftharpoons 2N + M$	$N_2 + M \rightleftharpoons 2N + M$	$O_2 + M \rightleftharpoons 20 + M$	$O_2 + M \rightleftharpoons 20 + M$	$NO + M \rightleftharpoons N + O + M$	$NO + M \rightleftharpoons N + O + M$	$\operatorname{Exchange}$	$N_2 + O \rightleftharpoons NO + N$	$NO + O \rightleftharpoons O_2 + N$