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Highlights

- Hypersonic non-equilibrium flows over rounded nose geometries are numerically investigated by a robust conservation element and solution element.
- The two-temperature model and the CV–CV chemical model have been implemented.
- Simulations were performed to calculate the heat transfer and chemical non-equilibrium.

Extension of CE/SE method to non-equilibrium dissociating flows

C.Y. Wen¹, H. Saldivar Massimi¹

¹*Department of Mechanical Engineering, The Hong Kong Polytechnic University, Kowloon, Hong Kong SAR*

and

Hua Shen²

²*King Abdullah University of Science and Technology (KAUST), Computer Electrical and Mathematical Science and Engineering Division (CEMSE), Extreme Computing Research Center (ECRC), Thuwal, Saudi Arabia*

Corresponding Author: cywen@polyu.edu.hk

Abstract

In this study, the hypersonic non-equilibrium flows over rounded nose geometries are numerically investigated by a robust conservation element and solution element (CE/SE) code, which is based on hybrid meshes consisting of triangular and quadrilateral elements. The dissociating and recombination chemical reactions as well as the vibrational energy relaxation are taken into account. The stiff source terms are solved by an implicit trapezoidal method of integration. Comparison with laboratory and numerical cases are provided to demonstrate the accuracy and reliability of the present CE/SE code in simulating hypersonic non-equilibrium flows.

Introduction

When a space vehicle enters the atmosphere at an orbital speed, a detached bow shock forms in front of its blunt nose and the temperature behind the shock, especially in the stagnation region, can reach high levels, due to the conversion of kinetic flow energy into thermal energy by strong shock compression. The important gas molecule dissociation and other real gas effects of hypersonic flows will occur. Consequently, the air can no longer be treated as a perfect gas and the dissociative non-equilibrium phenomenon complicates the flow physics¹.

Due to the extreme flow conditions, experimental approaches to study the hypervelocity flows are difficult in general, not to mention the expensive cost. Sometimes, inevitable large errors must be compromised. Theoretical methods are also limited in exploring the global dissociative non-equilibrium flow physics. Only some simple analytical solutions can be obtained, such as the dimensionless shock-off distance as a function of dimensionless dissociation rate²⁻⁴. Therefore, to thoroughly understand the hypersonic dissociative non-equilibrium flows, numerical studies are essential.

Because in the field of computational fluid dynamics (CFD) a conflict between stability and numerical accuracy is one that affects most of the established methods, Chang and To⁵ developed the space-time conservation element and solution element (CE/SE), using the unique approach of enforcing flux conservation in both space and time with extensive physics considerations. Since its inception in 1991, it has been used to obtain highly accurate numerical solutions for 1D, 2D, and 3D flow problems involving shocks, contact discontinuities, vortices, etc.⁵⁻⁸

Chang^{9, 10} and Chang and Choudhari¹¹ had successfully applied the CE/SE method to study viscous hypersonic flows without considering the non-equilibrium effects. The present work aims to extend the inviscid CE/SE code based on hybrid meshes consisting of triangular and quadrilateral elements^{12, 13} to solve hypersonic chemical reacting non-equilibrium flows. Both

chemical dissociation and vibrational energy relaxation are considered. The code is capable to use the CV-CV¹⁴ model developed by Knab and the two-temperature chemical kinetic model developed by Park¹⁵⁻¹⁷.

Cases of nitrogen, air and carbon dioxide are provided to demonstrate the accuracy and reliability of the method regarding non-equilibrium flows where the flow features of hypersonic flows are analyzed in detail and compared with the theoretical results. Furthermore, an Air flow case from Knab¹⁴ experiments was used to test the code capabilities regarding the coupled CV-CV model multiple vibrational temperature effects.

Governing Equations and Physical Model

Usually, high-speed flows are described by classic Navier-Stokes equations or inviscid Euler equations with a perfect gas equation of state. However, due to the high temperature effect, the important gas molecule dissociation, ionization and other real gas effects of hypersonic flows may occur. In addition, the high molecular energy mode, e.g. vibrational energy, will also be excited. Therefore, more terms must be added into the classic Navier-Stokes equations or Euler equations to take these phenomena into account and hence, the general form of the equations governing 2D reactive non-equilibrium flows with n_s species can be written as

$$\frac{\partial \mathbf{U}}{\partial t} + \frac{\partial \mathbf{F}(\mathbf{U})}{\partial x} + \frac{\partial \mathbf{G}(\mathbf{U})}{\partial y} - \Psi_v \left(\frac{\partial \mathbf{F}_v(\mathbf{U})}{\partial x} + \frac{\partial \mathbf{G}_v(\mathbf{U})}{\partial y} \right) = \Psi_s \mathbf{S}(\mathbf{U}) + \Psi_r \mathbf{R}(\mathbf{U}) \quad (1)$$

where $\mathbf{U} = [\rho_1, \dots, \rho_{n_s}, \rho u, \rho v, E, E_{v_{m_1}}, \dots, E_{v_{m_s}}]^T$ is the conservative quantity vector. $\mathbf{F}$ and $\mathbf{G}$ are the convection fluxes, which are given by

$$\mathbf{F} = [\rho_1 u, \dots, \rho_{n_s} u, \rho u^2 + p, \rho uv, (E + p)u, E_{v_{m_1}} u, \dots, E_{v_{m_s}} u]^T \quad (2)$$

and

$$\mathbf{G} = [\rho_1 v, \dots, \rho_{n_s} v, \rho uv, \rho v^2 + p, (E + p)v, E_{v_{m_1}} v, \dots, E_{v_{m_s}} v]^T \quad (3)$$

The viscid fluxes $\mathbf{F}_v$ and $\mathbf{G}_v$ can be expressed in the following form

$$\mathbf{F}_v = \begin{bmatrix} -\rho u_1^d \\ \vdots \\ -\rho u_{n_s}^d \\ \tau_{xx} \\ \tau_{xy} \\ \tau_{xx}u + \tau_{xy}v - q_x - q_x^v - \sum_{s=1}^{n_s} \rho_s u_s^d h_s \\ -q_x^v - \rho_{m_1} u_{m_1}^d e_{m_1}^v \\ \vdots \\ -q_x^v - \rho_{m_s} u_{m_s}^d e_{m_s}^v \end{bmatrix} \quad (4)$$

$$\mathbf{G}_v = \begin{bmatrix} -\rho v_1^d \\ \vdots \\ -\rho v_{n_s}^d \\ \tau_{xy} \\ \tau_{yy} \\ \tau_{yy}v + \tau_{xy}u - q_y - q_y^v - \sum_{s=1}^{n_s} \rho_s u_s^d h_s \\ -q_y^v - \rho_{m_1} v_{m_1}^d e_{m_1}^v \\ \vdots \\ -q_y^v - \rho_{m_s} v_{m_s}^d e_{m_s}^v \end{bmatrix} \quad (5)$$

$\mathbf{S}$ is the source term caused by symmetry (y being the axis of symmetry) and $\mathbf{R}$ is that caused by chemical reactions and energy relaxation. They can be expressed in the following form

$$\mathbf{S} = -\frac{1}{y} \begin{bmatrix} \rho_1 v \\ \vdots \\ \rho_{n_s} v \\ \rho uv \\ \rho v^2 \\ (E + p)v \\ E_{v_{m_1}} v \\ \vdots \\ E_{v_{m_s}} v \end{bmatrix} + \frac{\Psi_v}{y} \begin{bmatrix} -\rho v_1^d \\ \vdots \\ -\rho v_{n_s}^d \\ \tau_{xy} \\ \tau_{yy} - \tau_{\theta\theta} \\ \tau_{yy}v + \tau_{xy}u - q_y - q_y^v - \sum_{s=1}^{n_s} \rho_s u_s^d h_s \\ -q_y^v - \rho_{m_1} v_{m_1}^d e_{m_1}^v \\ \vdots \\ -q_y^v - \rho_{m_s} v_{m_s}^d e_{m_s}^v \end{bmatrix} \quad (6)$$

$$\mathbf{R} = \begin{bmatrix} \dot{\omega}_1 \\ \vdots \\ \dot{\omega}_{n_s} \\ 0 \\ 0 \\ 0 \\ \dot{\omega}_{v_{m_1}} \\ \vdots \\ \dot{\omega}_{v_{m_s}} \end{bmatrix} \quad (7)$$

In these expressions, $\rho_1 \dots \rho_{n_s}$ are the species densities, u and v are the bulk velocity components, E and $E_{v_{m_i}}$ are the total and the i -th molecule vibrational energy per unit volume of mixture, p is the pressure, τ_{ij} are the viscous stress components, q_i and q_i^v , are the translational-rotational and vibrational heat fluxes in the i -th direction. Moreover, h_s is the species enthalpy and $-\rho_i u_i^d$ and $-\rho_i v_i^d$ are the i -species diffusion flux in the x and y direction respectively, $\dot{\omega}_s$ is the mass production/destruction term for chemical species s and $\dot{\omega}_{v_{m_i}}$ is the i -th molecule vibrational energy source term. Finally, Ψ_v is a switch function with values of 0 and 1 for inviscid and viscous problems, respectively; Ψ_s is a switch function and has values of 0 and 1 for two-dimensional and axisymmetric three-dimensional problems, respectively; while Ψ_r is also a switch function and has values of 0 and 1 for chemical reacting and frozen gas cases, respectively.

Under Stokes' hypothesis of negligible bulk viscosity effects, the viscous stresses can be expressed as follows:

$$\tau_{xx} = 2\mu \frac{\partial u}{\partial x} - \frac{2}{3}\mu \left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \psi_s \frac{v}{y} \right) \quad (8)$$

$$\tau_{yy} = 2\mu \frac{\partial v}{\partial y} - \frac{2}{3}\mu \left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \psi_s \frac{v}{y} \right) \quad (9)$$

$$\tau_{xy} = \tau_{yx} = \mu \left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} \right) \quad (10)$$

$$\tau_{\theta\theta} = -\frac{2}{3}\mu \left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + 2\frac{v}{y} \right) \quad (11)$$

Here, $\tau_{\theta\theta}$ is the viscous stress component in the circumferential direction θ the i -species diffusion flux is assumed to be proportional to the gradients of the mass fractions

$$\rho_i u_i^d = -\rho D_i \frac{\partial c_i}{\partial x} \quad (12)$$

and

$$\rho_i v_i^d = -\rho D_i \frac{\partial c_i}{\partial y} \quad (13)$$

The heat fluxes appeared in the viscous fluxes are modeled per Fourier's law as

$$q_{Tr,V} = -\kappa_{Tr,V} \nabla T_{Tr,V} \quad (14)$$

where $\kappa_{Tr,V}$ are the mixture thermal conductivity for each energy mode.

The mixture pressure p is obtained using Dalton's law of partial pressures and the perfect gas law for each species. Thus, $p = \sum_{s=1}^{n_s} \frac{\rho_s R_u}{M_s} T$ where R_u is the universal gas constant.

The combined energy in the translational and rotational modes is obtained by subtracting the vibrational, kinetic, and chemical energies from the total energy. Assuming that the rotational energy modes are in equilibrium with the translational modes, the caloric equation of state for mass-averaged gas is derived as

$$\sum_{s=1}^{n_s} \rho_s c_s^v T = E - \sum_{s=1}^{m_s} E_{v_{m_s}} - \frac{1}{2} \rho (u^2 + v^2) - \sum_s^n \rho_s h_s \quad (15)$$

where, c_s^v and h_s are the translational-rotational specific heat at constant volume and species enthalpy, respectively.

Transport Properties

Wilke's mixing rule¹⁸ is used to calculate the transport properties of the gas:

$$\mu = \sum_s \frac{X_s \mu_s}{\phi_s}$$

$$\kappa = \sum_s \frac{X_s \kappa_s}{\phi_s}$$

where μ and κ are viscosity and thermal conductivity of the gas, respectively, X_s is the species molar fraction, μ_s is the species coefficient of viscosity and κ_s is the species thermal conductivity. The term ϕ_s is given by

$$\phi_s = \sum_r X_r \left[1 + \sqrt{\frac{\mu_s}{\mu_r}} \left(\frac{M_r}{M_s} \right)^{\frac{1}{4}} \right]^2 \left[\sqrt{8 \left(1 + \frac{M_s}{M_r} \right)} \right]^{-1}$$

The species viscosities are calculated using Blottner's curve fits¹⁹

$$\mu_s = 0.1 \exp[(A_s \ln T + B_s) \ln T + C_s]$$

where A_s , B_s and C_s are constants determined for each species²⁰. The species thermal conductivities are determined using Eucken's relation²¹ as

$$\kappa_{tr,s} = \frac{5}{2} \mu_s c_s^t + \mu_s c_s^r$$

Chemical Model

Chemical model plays an important role in the accurate description of composition of the high-temperature gas. Several investigators have discussed the problems of chemical non-equilibrium in the shock layers over vehicles flying at high speeds and high altitudes in Earth's atmosphere.

For Nitrogen flows, only two species (N₂ and N) and two chemical reactions are used, for CO₂ and airflows, five species ((CO₂, O₂, CO, C and O) and (N₂, O₂, NO, N and O) respectively) and seventeen reactions are considered. The chemical reaction parameters used can be found in references 15-17.

The mass production/destruction term for chemical species $\dot{\omega}_s$ is formulated as

$$\dot{\omega}_s = M_s \sum_{r=1}^{n_r} (\beta_{sr} - \alpha_{sr}) \left[k_{fr} \prod_{j=1}^{n_s} \left(\frac{\rho_j}{M_j} \right)^{\alpha_{jr}} - k_{br} \prod_{j=1}^{n_s} \left(\frac{\rho_j}{M_j} \right)^{\beta_{jr}} \right] \quad (16)$$

where α and β are the stoichiometric coefficients of species s in reaction r . The forward and backward reaction rates are affected by the level of non-equilibrium in the flow. To account for that effect, Park's two-temperature model¹⁵⁻¹⁷ and CV-CV¹⁴ model can be used.

A. Two Temperature Model

For fast results, certain computer codes for calculating the non-equilibrium reacting flow use

the one-temperature model, which assumes that all the internal energy modes of the gaseous species are in equilibrium with the translational mode.

It has been pointed out that such a one-temperature description of the flow leads to a substantial overestimation of the rate of equilibration when compared with the existing experimental data. A three-temperature chemical-kinetic model has been proposed by Lee²² to describe the relaxation phenomena correctly in such a flight regime. However, the model is complex and requires many chemical rate parameters that are yet unknown. As a compromise between the three-temperature chemical-kinetic and the conventional one-temperature model, a two-temperature chemical-kinetic model has been developed by Park¹⁵⁻¹⁷. The model uses one temperature, T , to characterize the translational energy of the atoms and molecules and the rotational energy of the molecules, and another temperature, T_v , to characterize the vibrational energy of the molecules, translational energy of the electrons, and electronic excitation energy of atoms and molecules.

The forward reaction rates coefficients k_{fr} can be calculated by the Arrhenius' law as

$$k_{fr}(T) = A_{fr} T_c^{\eta_r} \exp\left(-\frac{\theta_r}{T_c}\right) \quad (17)$$

where the control temperature, T_c , can be the translational temperature T , the vibrational temperature T_v or a geometrical mean temperature, $\bar{T} = T^s T_v^{s-1}$, where s is between 0.5-0.7, no clear advantage of 0.7 over the 0.5 has yet been demonstrated^{23, 24}. The backward reaction rates depend only on the translational temperature as

$$k_{br}(T) = \frac{k_{fr}(T)}{K_{eq}(T)} \quad (18)$$

For air and nitrogen flows, the equilibrium constants can be obtained from

$$K_{eq}(T) = \exp\left[A_1 \frac{T}{10,000} + A_2 + A_3 \ln \frac{10,000}{T} + A_4 \frac{10,000}{T} + A_5 \left(\frac{10,000}{T}\right)^2\right] \quad (19)$$

were the coefficients A_i being a function of the local number density can be found in reference 25. For carbon dioxide flows, due to a lack of information regarding the coefficients A_i , the equilibrium constants are obtained from

$$K_{eq}(T) = \left(\frac{p_o}{RT_{tr}}\right)^{v_r} \exp - \sum_s (\beta_{s,r} - \alpha_{s,r}) \left[\frac{\hat{h}_s}{RT_{tr}} - \frac{\hat{s}_s}{R}\right] \quad (20)$$

ere p_o is a reference pressure set to 1 bar and $v_r = \sum_s (\beta_{s,r} - \alpha_{s,r})$. The normalized enthalpy and entropy are obtained from curve fits of the form

$$\frac{\hat{h}_s}{RT_{tr}} = -\frac{B_1}{T^2} + B_2 \frac{\ln(T)}{T} + B_3 + B_4 \frac{T}{2} + B_5 \frac{T^2}{3} + B_6 \frac{T^3}{4} + B_7 \frac{T^4}{5} + \frac{B_8}{T} \quad (21)$$

$$\frac{\hat{s}_s}{R} = -\frac{B_1}{2T^2} + B_2 \frac{1}{T} + B_3 \ln(T) + B_4 T + B_5 \frac{T^2}{2} + B_6 \frac{T^3}{3} + B_7 \frac{T^4}{4} + B_9 \quad (22)$$

where the coefficients B_i are a function of temperature and can be found in reference 26.

B. CV-CV

The first quantitative multi-temperature approach based on state selective rates together with the Boltzmann distribution for internal energy was proposed by Hammerling²⁷ in 1959. Treanor and Marrone²⁸ extended this model, including the reverse effect that dissociation exerts on the vibrational relaxation rate. To describe the influence of vibration on exchange reactions and associative ionization reactions as well as the coupling of the reactions on vibrational energy, the CVCV model was proposed by Knab¹⁴.

In Knab's model, the thermal equilibrium reaction rates are modified using an efficiency function $\varphi(T, T_v)$ as follows

$$k(T, T_v) = \varphi(T, T_v) k_{eq}(T) \quad (23)$$

The efficiency function is calculated disregarding any harmonicity effects, using the trunked harmonic oscillator model,

$$Q(T, E) = \frac{1 - e^{-\frac{E}{RT}}}{1 - e^{-\frac{\theta_v}{T}}} \quad (24)$$

where θ_v and E are the characteristic vibrational temperature and the truncated maximum energy respectively. The efficiency function is computed as

$$\varphi(T, T_v) = X_1 \frac{X_2}{X_3} \quad (25)$$

where

$$X_1 = \frac{Q(T, E_d)}{Q(T_v, E_d)} \quad (26)$$

$$X_2 = e^{-\alpha \frac{E_d}{RT}} Q(\Gamma, \alpha E_d) + Q(T^0, E_d) - Q(T^0, \alpha E_d) \quad (27)$$

$$X_3 = e^{-\alpha \frac{E_d}{RT}} Q(-U, \alpha E_d) + Q(T^*, E_d) - Q(T^*, \alpha E_d) \quad (28)$$

E_d is the dissociation energy of the molecule, E_a is the activation energy for the reaction, α is a coefficient that determines the fraction of energy required for each reaction and is set to 0.7-0.8. T^0 , T^* , Γ and U are temperatures defined as,

$$\frac{1}{\Gamma} = \frac{1}{T_v} - \frac{1}{T} - \frac{1}{U} \quad (29)$$

$$U = \frac{E_d}{5R} \quad (30)$$

$$\frac{1}{T^0} = \frac{1}{T_v} - \frac{1}{U} \quad (31)$$

$$\frac{1}{T^*} = \frac{1}{T} - \frac{1}{U} \quad (32)$$

C. Relaxation Model

The vibrational energy source term $\dot{\omega}_{v_{m_i}}$ is given by

$$\dot{\omega}_{v_{m_i}} = S_{c-v} + S_{t-v} + S_{v-v} \quad (33)$$

where S_{c-v} is the vibrational-electron-electronic energy added, or removed by chemical reactions modelled using a non-preferential model where it is assumed that molecules are created or destroyed at the average vibrational energy, hence

$$S_{c-v} = \sum_s \dot{\omega}_s e_{v,s} \quad (34)$$

S_{v-v} is to account for vibration-vibration energy exchange¹⁰ given by

$$S_{v-v} = N_a \sqrt{\frac{8R_u T}{\pi M_u}} \sum_{s \neq i}^{m_s} 0.01 \sigma_s \frac{c_i c_s}{\sqrt{\mu_{is}}} \left(\frac{e_{v,i}^*(T)}{e_{v,r}^*(T)} e_{v,r}^*(T_v) - e_{v,i}^*(T_v) \right) \quad (35)$$

where, σ_s is the limiting cross section, $c_{i,s}$ are the i -th and s -th species mass fractions and μ_{is} is given by $\mu_{is} = \frac{M_i M_s}{M_i + M_s}$.

S_{t-v} is the energy exchange rate between the vibrational and translational modes modelled by the Landau-Teller model¹⁸ as

$$S_{t-v} = \sum_{s=1}^{n_s} \rho_s \frac{e_{v,s}^*(T) - e_{v,s}(T_v)}{\tau_s} \quad (36)$$

where

$$\tau_s = \langle \tau_s \rangle + \tau_{ps} \quad (37)$$

The molar averaged Landau-Teller relaxation time, $\langle \tau_s \rangle$ is written as

$$\langle \tau_s \rangle = \frac{\sum_{r=1}^{n_s} X_r}{\sum_{r=1}^{n_s} \frac{X_r}{\tau_{sr}}} \quad (38)$$

where, X_r is the molar fraction of species r . The Landau-Teller relaxation time between species s and r , τ_{sr} , can be modelled using curve fits given by Millikan and White¹⁷ for vibrational relaxation as

$$\tau_{sr} = \frac{101,325}{p} \exp \left[A_{sr} \left(T^{\frac{1}{3}} - B_{sr} \right) - 18.42 \right] \quad (39)$$

The values for A_{sr} and B_{sr} are derived by using tabulated data from Hash et al²⁹. It is known that Millikan and White curve underestimate the relaxation time at high temperatures. Park²³ corrected this problem by limiting the collision cross section and adding the corresponding limiting relaxation time

$$\tau_{ps} = \frac{1}{\sigma_s a_s N} \quad (40)$$

to fix this problem, where N is the number density of the mixture, as is the average molecular speed of the species which is given by

$$a_s = \sqrt{\frac{8R_u T}{\pi M_s}} \quad (41)$$

and σ_s is the limiting cross section defined as

$$\sigma_s = 10^{-20} \left(\frac{50,000}{T} \right)^2 m^2 \quad (42)$$

The above energy relaxation model is only applicable for nitrogen and air flows. For CO₂ flows, results of Camac³⁰ indicate that due to strong resonance coupling between the different vibrational modes of CO₂ the three vibrational modes of CO₂ relax at the same rate, and the vibrational relaxation time of CO₂ can be modelled by

$$\tau_{CO_2} = \frac{1}{p_{atm}} \exp \left(36.5 T^{-\frac{1}{3}} - 17.71 \right) \quad (43)$$

where p_{atm} is pressure in atmospheres.

Numerical Algorithm

A. Review of CE/SE Scheme Based on Hybrid Meshes

In the present work, a robust CE/SE scheme based on hybrid meshes^{12, 13} is used to solve the governing equation and hence, we simply review the scheme in the following.

To simplify the mathematical expression, we define

$$u \equiv U, f \equiv F - \Psi_v F_v, g \equiv G - \Psi_v G_v \text{ and } s \equiv \Psi_s S \quad (44)$$

Equation (1) is then simplified as

$$\frac{\partial u}{\partial t} + \frac{\partial f}{\partial x} + \frac{\partial g}{\partial y} = s \quad (45)$$

The source term caused by chemical reactions and energy relaxation R will be treated separately later.

Considering the spatial coordinates x and y together with t be the new coordinates of a Euclidean space E_3 , and then Eq. (45) can be expressed as $\nabla \cdot h_m = s_m$ ($m=1$ to n_s+4), where $h_m=(f_m, g_m, u_m)$. According to Gauss' divergence theorem, Eq. (45) is the differential form of the integral conservation law

$$\oint_{S(V)} h_m \cdot ds = \iiint_V s_m dV \quad (46)$$

where $S(V)$ is the boundary of an arbitrary closed space-time region V in E_3 , and $ds=d\sigma n$, in which $d\sigma$ and n are the area and unit outward normal vector of a micro surface element on $S(V)$, respectively.

Figure 1. Hybrid mesh and definition of CE and SE

To proceed, the spatial domain is divided into hybrid meshes which consist of triangular elements and quadrilateral elements, as shown by Fig. 1(a). The solid lines represent the original mesh lines. For the convenience of expression, the following notations are adopted:

- V_i the i th vertex (marked by solid circles);
 A_i the i th mid-point of the element edges (marked by hollow circles);
 C_i the i th centroid of the original elements (marked by solid squares);
 G_i the i th centroid of staggered elements (marked by solid triangles). For example, G_1 is the centroid of the staggered element $A_1C_5A_3C_1A_6C_2A_8C_3A_{10}C_4$;
 P' the point at time level $t=t^{n+1/2}$ corresponding to P ;
 P'' the point at time level $t=t^{n+1}$ corresponding to P ;
 P^* the point at time level $t=t^{n+3/2}$ corresponding to P .

The staggered time marching strategy is adopted in present scheme, i.e., the solution is updated alternatively between element center (marked by solid squares) and element vertexes (marked by solid circles). We define a conservation element (CE) and a solution element (SE) for each solution point is very important. In a hybrid mesh, the corresponding spatial elements for solution points C_i are triangles or quadrangles, while for solution points V_i (or G_i), the corresponding spatial elements could be arbitrary shape of polygons. The configurations of the CE and SE for different shapes of elements are slightly different but essentially identical, which are respectively defined as follows:

- (a) As shown in Fig. 1(b), CE(C_1') for the triangular element $V_1V_2V_3$ is defined by the triangular prism $V_1V_2V_3V_1'V_2'V_3'$, while SE(C_1') is defined by four planes, i.e., $V_1'V_2'V_3'$, $A_1C_1C_1''A_1''$, $A_2C_1C_1''A_2''$ and $A_3C_1C_1''A_3''$, intersecting at C_1' and the triangular prism $V_1'V_2'V_3'V_1''V_2''V_3''$.
(b) Similarly, CE(C_1') for quadrilateral element $V_1V_2V_3V_4$ is defined by the hexahedron $V_1V_2V_3V_4V_1'V_2'V_3'V_4'$, while SE(C_1') is constituted by five planes, namely $V_1'V_2'V_3'V_4'$, $A_1C_1C_1''A_1''$, $A_2C_1C_1''A_2''$, $A_3C_1C_1''A_3''$ and $A_4C_1C_1''A_4''$, intersecting at C_1' and the hexahedron $V_1'V_2'V_3'V_4'V_1''V_2''V_3''V_4''$ (see Fig. 1(c)).
(c) CE(V_i'') for an arbitrary polygonal element $C_1A_1...C_KA_K$ is defined by the polyhedron $C_1'A_1'...C_K'A_K'C_1''A_1''...C_K''A_K''$, and SE(V_i'') is constituted by $K+1$ planes, namely $C_1''A_1''...C_K''A_K''$, $A_1'V_i'V_i^*A_1^*$, ..., and $A_K'V_i'V_i^*A_K^*$, intersecting at V_i'' and the polyhedron $C_1''A_1''...C_K''A_K''C_1^*A_1^*...C_K^*A_K^*$ (see Fig. 1(d)). K is the number of elements related to V_i . For convenience, points C_1 , C_K and A_K are also denoted as C_{K+1} , C_0 and A_0 , respectively.

Notably, compared with the definition of SE¹², there is an additional volume (e.g. the triangular prism $V_1'V_2'V_3'V_1''V_2''V_3''$ for triangular element) for solving the source term.

Imposing the conservation law of Eq. (46) on CE(V_i'') yields

$$\iint_{C_1'A_1'...C_K'A_K'} u_m d\sigma = \sum_{k=1}^K \iint_{C_k'A_k'A_k''C_k''+C_k'A_{k-1}'A_{k-1}''C_k''} u_m d\sigma - \sum_{k=1}^K \iint_{C_k'A_k'A_k''C_k''+C_k'A_{k-1}'A_{k-1}''C_k''} (f_m n_x + g_m n_y) d\sigma + \iiint_{CE(V_i'')} s_m dV \quad (47)$$

where n_x and n_y are the components of the normal vector of corresponding surface. To solve the integral terms in Eq.(47), it is assumed that u_m , f_m , g_m and s_m in each SE are approximated by first order Taylor expansion. That is to say the distributions of u_m , f_m , g_m and s_m are all linear in CE(V_i'') and its boundary surfaces affiliated to SE(C_1'), ..., SE(C_K') and SE(V_i''), respectively. Thus, the integrations of $(u_m, f_m, \text{ and } g_m)/s_m$ on/over any particular surface/volume are simply equivalent to the corresponding area/volume multiplied by the values of $(u_m, f_m, \text{ and } g_m)/s_m$ at the centroid, i.e.,

$$\iint_{C_1'A_1'...C_K'A_K'} u_m d\sigma = u_m(G_i'') \text{Area}(C_1''A_1''...C_K''A_K'') \quad (48)$$

$$\sum_{k=1}^K \iint_{C_k'A_k'A_k''C_k''+C_k'A_{k-1}'A_{k-1}''C_k''} u_m d\sigma = \sum_{k=1}^K u_m(\bar{G}_k') \text{Area}(C_k'A_k'V_i'A_{k-1}') \quad (49)$$

$$\sum_{k=1}^K \iint_{C_k'A_k'A_k''C_k''+C_k'A_{k-1}'A_{k-1}''C_k''} (f_m n_x + g_m n_y) d\sigma = \sum_{k=1}^K [FLUX_{m1}^{(k)} + FLUX_{m2}^{(k)}] \quad (50)$$

$$\iiint_{CE(V_i'')} s_m dV = \Delta t_{n+1/2} \sum_{k=1}^K s_m(G_k^*) \text{Area}(C_k' A_k' V_i' A_{k-1}') \quad (51)$$

where $\bar{G}_k'$ and G_k^* are the centroid of quadrangle $C_k' A_k' V_i' A_{k-1}'$ and hexahedron $C_k' A_k' V_i' A_{k-1}' C_k'' A_k'' V_i'' A_{k-1}''$ which belong to $\text{SE}(C_k')$. Therefore, $u(\bar{G}_k')$ and $u(G_k^*)$ can be calculated via the Taylor expansion in $\text{SE}(C_k')$. In addition, $FLUX_{m1}^{(s)}$ and $FLUX_{m2}^{(s)}$ represent the fluxes leaving surfaces $C_k' A_k' A_k'' C_k''$ and $C_k' A_{k-1}' A_{k-1}'' C_k''$, respectively, and are computed as

$$FLUX_{m1}^{(k)} = \Delta t_{n+1/2} \Delta y_1^{(k)} [f_m(C_k') + f_{mx}(C_k') \frac{\Delta x_1^{(k)}}{2} + f_{my}(C_k') \frac{\Delta y_1^{(k)}}{2} + f_{mt}(C_k') \frac{\Delta t_{n+1/2}}{2}] \\ - \Delta t_{n+1/2} \Delta x_1^{(k)} [g_m(C_k') + g_{mx}(C_k') \frac{\Delta x_1^{(k)}}{2} + g_{my}(C_k') \frac{\Delta y_1^{(k)}}{2} + g_{mt}(C_k') \frac{\Delta t_{n+1/2}}{2}] \quad (52)$$

$$FLUX_{m2}^{(k)} = \Delta t_{n+1/2} \Delta y_2^{(k)} [f_m(C_k') - f_{mx}(C_k') \frac{\Delta x_2^{(k)}}{2} - f_{my}(C_k') \frac{\Delta y_2^{(k)}}{2} + f_{mt}(C_k') \frac{\Delta t_{n+1/2}}{2}] \\ - \Delta t_{n+1/2} \Delta x_2^{(k)} [g_m(C_k') - g_{mx}(C_k') \frac{\Delta x_2^{(k)}}{2} - g_{my}(C_k') \frac{\Delta y_2^{(k)}}{2} + g_{mt}(C_k') \frac{\Delta t_{n+1/2}}{2}] \quad (53)$$

where,

$$\Delta x_1^{(k)} = x_{A_k} - x_{C_k}, \quad \Delta y_1^{(k)} = y_{A_k} - y_{C_k}, \\ \Delta x_2^{(k)} = x_{C_k} - x_{A_{k-1}}, \quad \Delta y_2^{(k)} = y_{C_k} - y_{A_{k-1}},$$

and

$$\Delta t_{n+1/2} = t_{n+1} - t_{n+1/2}.$$

Finally, substituting Eqs. (48) - (51) into Eq. (49), along with Eqs. (52) and (53), an explicit time marching scheme for $u_m(G_i'')$ is obtained as

$$u_m(G_i'') = \frac{\sum_{k=1}^K u_m(\bar{G}_k) \text{Area}(C_k' A_k' V_i' A_{k-1}') - \sum_{k=1}^K (FLUX_{m1}^{(k)} + FLUX_{m2}^{(k)}) + \Delta t_{n+1/2} \sum_{k=1}^K s_m(G_k^*) \text{Area}(C_k' A_k' V_i' A_{k-1}')}{\text{Area}(C_1 A_1 \dots C_K A_K)} \quad (54)$$

In the first-order Taylor expansion, besides u_m itself, its first-order derivatives are also unknown. Substituting the first-order Taylor expansion into Eq.(45), one can obtain

$$\frac{\partial u_m}{\partial t} = -\frac{\partial f_m}{\partial x} - \frac{\partial g_m}{\partial y} + s_m \quad (55)$$

Therefore, we must update u_m , u_{mx} and u_{my} at each solution point. As shown by Fig. 1(d), C_k'' ($k=1 \sim K$) belongs to both $\text{SE}(G_i'')$ and $\text{SE}(C_k')$. Therefore, $u_m(C_k'')$ can be calculated through Taylor expansion in $\text{SE}(G_i'')$ and $\text{SE}(C_k')$, i.e.,

$$u_m(C_k') + u_{mt}(C_k') \Delta t_{n+1/2} = u_m(C_k'') = u_m(G_i'') + u_{mx}(G_i'') \delta x_k + u_{my}(G_i'') \delta y_k, \quad (56)$$

where

$$\delta x_k = x_{C_k} - x_{G_i}, \quad \text{and} \quad \delta y_k = y_{C_k} - y_{G_i}.$$

The same relation can be derived for $k+1$ as

$$u_m(C_{k+1}') + u_{mt}(C_{k+1}') \Delta t_{n+1/2} = u_m(C_{k+1}'') = u_m(G_i'') + u_{mx}(G_i'') \delta x_{k+1} + u_{my}(G_i'') \delta y_{k+1}. \quad (57)$$

Note that, $u_m(G_i'')$ has already been calculated by Eq. (54), so Eqs. (55) and (56) are linear equations with two unknowns $u_{mx}(G_i'')$ and $u_{my}(G_i'')$. Define

$$\delta u_m^{(k)} \equiv u_m(C_k') + u_{mt}(C_k') \Delta t_{n+1/2} - u_m(G_i'').$$

Then, one pair of derivatives (defined as $u^{(k)}_{mx}(G_i'')$ and $u^{(k)}_{my}(G_i'')$, respectively) can be calculated using Cramer's rule as

$$u_{mx}^{(k)}(G_i'') = \frac{\Delta_{mx}^{(k)}}{\Delta_m^{(k)}}, \quad u_{my}^{(k)}(G_i'') = \frac{\Delta_{my}^{(k)}}{\Delta_m^{(k)}}, \quad (58)$$

where

$$\Delta_m^{(k)} = \begin{vmatrix} \delta x_k & \delta y_k \\ \delta x_{k+1} & \delta y_{k+1} \end{vmatrix}, \quad \Delta_{mx}^{(k)} = \begin{vmatrix} \delta u_m^{(k)} & \delta y_k \\ \delta u_m^{(k+1)} & \delta y_{k+1} \end{vmatrix}, \quad \Delta_{my}^{(k)} = \begin{vmatrix} \delta x_k & \delta u_m^{(k)} \\ \delta x_{k+1} & \delta u_m^{(k+1)} \end{vmatrix}. \quad (59)$$

Totally, K pairs of derivatives can be obtained in this way. Thereafter, $u_{mx}(G_i'')$ and $u_{my}(G_i'')$ can be evaluated by the average of the K pairs of derivatives as

$$u_{mx}(G_i'') = \frac{1}{K} \sum_{k=1}^K u_{mx}^{(k)}(G_i''), \quad u_{my}(G_i'') = \frac{1}{K} \sum_{k=1}^K u_{my}^{(k)}(G_i''). \quad (60)$$

Alternatively, for a problem with discontinuities, a simple weighted average function can be used as a limiter, i.e.,

$$u_{mx}(G_i'') = \sum_{k=1}^K W_m^{(k)} u_{mx}^{(k)}(G_i'') / (\sum_{k=1}^K W_m^{(k)} + \zeta), \quad (61)$$

$$u_{my}(G_i'') = \sum_{k=1}^K W_m^{(k)} u_{my}^{(k)}(G_i'') / (\sum_{k=1}^K W_m^{(k)} + \zeta), \quad (62)$$

where

$$W_m^{(k)} = \left(\prod_{j=1, j \neq k}^K \theta_m^{(j)} \right)^{\chi}, \quad k = 1 \sim K \quad (63)$$

with

$$\theta_m^{(j)} = \sqrt{[u_{mx}^{(j)}(G_i'')]^2 + [u_{my}^{(j)}(G_i'')]^2}, \quad j = 1 \sim K. \quad (64)$$

Here, $\chi \geq 0$ is an adjustable parameter used to control the dissipations near discontinuities in the computational domain. For the second-order CE/SE scheme, χ is usually assigned a value in the range of 0~2. When χ increases, the dissipations also increase. When $\chi=0$, the dissipations are the lowest and Eqs. (61) and (62) are equivalent to the simple average function expressed by Eq. (60). Furthermore, to avoid dividing by zero, a small positive number (e.g., $\zeta = 10^{-60}$) is added to the denominators.

At last, we must notice that the solution points C_i' at $t_{n+1/2}$ are exactly located at the centers of original elements where the solutions can be directly updated by Eqs. (54), (61) and (62) ($K=3$ and 4 for triangular and quadrilateral elements, respectively). However, the solution points V_i'' at t_{n+1} may not coincide with the centers of the staggered elements G_i'' . Consequently, once $u_m(G_i'')$ and its spatial derivatives have been computed through Eqs. (54), (61) and (62), $u_m(V_i'')$ must be updated via the Taylor expansion and its spatial derivatives are equal to $u_{mx}(G_i'')$ and $u_{my}(G_i'')$.

B. Treatment of Stiff Source Term

The CE/SE is only used to solve the flow dynamics and the source term caused by chemical reactions and energy relaxation $\mathbf{R}$ (Eq. (7)) is treated separately. The rationale behind this is that the CE/SE scheme is an explicit scheme and its time step is limited by the CFL condition ($CFL \leq 1$). The source terms involving chemical reactions or energy exchange rates may cause the stiffness problem, i.e., the rates may be orders of magnitude higher than the flow velocity. Therefore, if we solve the stiff source terms together with the flow using the explicit CE/SE scheme, the time step may be limited to a very small range due to the limitation of the CFL

condition. To overcome this problem, the reacting and energy exchange source term is solved by an implicit trapezoidal method of integration, which is expressed in as

$$\left(I - \Delta t \left[\frac{\partial \mathbf{R}}{\partial \mathbf{U}} \right]^n \right) (\mathbf{U}^{n+1} - \mathbf{U}^n) = \Delta t \mathbf{R}^n$$

where $\partial \mathbf{R} / \partial \mathbf{U}$ is the Jacobi matrix of the stiff reacting source term $\mathbf{R}$. $\mathbf{I}$ and $\mathbf{U}$ are unit matrix and conservative quantity vector, respectively. Due to the inherent nature of the CE/SE method, the physical quantities and their derivative are solved simultaneously. Therefore, the process to calculate the viscous flux is straightforward.

Figure 2. Schematic of computational model (a), Speed distribution along the stagnation streamline for case 9 using different mesh sizes (b), and typical grid used for viscous cases (c).

RESULTS

A. Simulation Model

When the hypersonic flow encounters a sphere, a bow shock will detach from the surface of the sphere. The shape of the bow shock and the distance between the shock and body on the stagnation line, namely the shock stand-off distance, Δ , are two important flow characteristics. Besides focusing on these two flow features the present study will pay attention to the non-equilibrium effects and heat transfer. The flow is assumed to be axisymmetric, such that the computational domain is reduced to only one-half of the complete flow field. As shown in Fig. 2, uniform supersonic freestream conditions are imposed on the left boundary. A zero-gradient non-reflective boundary conditions are implemented on the right side. Depending on the test case, an adiabatic free-slip boundary condition, or an isothermal non-catalytic wall boundary condition are applied on the surface of the spheres.

Finally, the symmetric boundary condition is applied to the lower boundary. Grid-independence tests were carefully performed. This was achieved by running a series of simulations by increasing the mesh size by a factor of 1.5 until the difference in the stagnation streamline properties between mesh models was smaller than 2%. Figure 2(b) shows the speed distribution along the stagnation streamline for case 9 using different mesh sizes. Density and pressure distributions for all the cases of this study also show similar convergence with their mesh size.

Notably, even though the code could handle hybrid and triangular meshes, this study utilized a quadrilateral structural computational grid made of 6,240 and 62,000 cells for inviscid and viscous cases, respectively (Fig. 2(c)). The quadrilateral meshes that are tailored and aligned with the shock were used due to the geometric simplicity of the studied spherical object and to avoid issues related with strong bow shocks. Similar situations occur in the boundary layer. If the shock was not aligned or if triangular mesh was used in place of the quadrilateral, the code

would need to run with an extremely fine mesh to prevent issues related to strong bow shocks, making the simulations highly inefficient and costly.

The majority of the simulations were performed using a custom-built work-station. To increase the computational efficiency and reduce the workload, the code was parallelized using OpenMP. Total CPU hours for an inviscid simulation and a viscous one are about 12 and 48 hours, respectively.

B. Nitrogen Flows

Table 1. Freestream conditions of nitrogen flow cases selected from Wen & Hornung²

Case No.	R (inch)	ρ_∞ (kg/m ³)	u_∞ (m/s)	T_∞ (K)	α_∞
1	0.5	0.0374	5150	2340	0.036
2	1	0.0198	4860	1950	0.041
3	1.5	0.0195	5140	2200	0.064
4	2	0.0181	5350	2350	0.090

Table 2. Experimental, theoretical and numerical dimensionless shock stand-off distance, $\bar{\Delta}$, for nitrogen flows

Case No.	Experiment (Wen & Hornung ²)	Theory (Wen & Hornung ²)	Simulation
1	0.096	0.095	0.101
2	0.114	0.099	0.109
3	0.100	0.095	0.100
4	0.099	0.094	0.099

Nitrogen flow is one of the simplest hypersonic dissociating flows. If there is no ionization, only two species exist in the flow. Therefore, nitrogen flow has been widely investigated by previous researchers. In present study, we first apply the CE/SE code to simulate the experimental nitrogen flow cases selected from Wen & Hornung², where the hypervelocity flows over spheres of various radii and freestream conditions were studied. The sphere radii and freestream conditions of selected cases are listed in table 1 and the comparison of experimental, theoretical and numerical dimensionless shock-off distances $\bar{\Delta} \equiv \Delta/R$ are listed in table 2. Here, the theoretical results are calculated by Wen & Hornung's theory which is based on the fact that the oncoming mass flow entering the shock has to leave the flow field between shock and body. This theory gives an analytic solution for the whole non-equilibrium flow regime without use any specific gas model and is presented by a piecewise function as²

$$\bar{\Delta} = \begin{cases} \frac{1}{\tilde{\Omega}} \left[-1 + \sqrt{1 + 2L\tilde{\Omega}} \right], & \text{when } \rho_b < \rho_e, \\ \frac{\rho_{sh}}{\rho_e} \left[L + \frac{1}{2\tilde{\Omega}} \left(\frac{\rho_e}{\rho_{sh}} - 1 \right)^2 \right], & \text{else.} \end{cases}$$

Here, the constant L equals to 0.41 for spheres which is given by the well-known Lobb's³¹ correlation for supersonic frozen flows. $\tilde{\Delta}$ is another dimensionless shock-off distance which is defined as

$$\tilde{\Delta} \equiv \frac{1}{2} \frac{\Delta}{R} \frac{\rho_{sh}}{\rho_\infty}.$$

The generalized dimensionless reaction rate parameter $\tilde{\Omega}$ is defined by

$$\tilde{\Omega} \equiv \left(\frac{d\rho}{dt} \right)_{sh} \frac{D}{\rho_{sh} u_\infty}.$$

At the first glance, $\tilde{\Omega}$ represents the density variation right after the shock on the stagnation streamline when the flow passes the sphere. However, Wen & Hornung² deepened physical significance of $\tilde{\Omega}$ as

$$\tilde{\Omega} = \frac{\text{Energy absorption rate by chemistry}}{\text{Input rate of free stream kinetic energy}}$$

Form table 2, we can see that the present numerical results agree very well with Wen & Hornung's experimental and theoretical results. The largest error between the results of simulation and experiments is about 5%. To further compare the numerical results with Wen & Hornung's experimental results, we compare the bow shock shapes by overlapping the numerical density contours in the experimental finite fringe differential interferograms in Fig. 3. It is shown that the shapes of the numerical bow shocks fit the experimental results very well. It demonstrated that the present code is reliable for simulating hypersonic dissociating flows.

Figure 3. Comparison of the numerical and experimental shapes of the bow shocks for nitrogen flows.

Figure 4. Comparison of dimensionless shock stand-off distance for nitrogen flow

To thoroughly study the influence of the important parameter $\tilde{\Omega}$ on the flow features of hypersonic dissociating flows, we choose one typical set of freestream condition as $\rho_{\infty}=0.0443\text{kg/m}^3$, $u_{\infty}=5200\text{kg/m}^3$, $T_{\infty}=2300\text{K}$ and $\alpha_{\infty}=0.0156$. The radii of spheres are varied to obtain different $\tilde{\Omega}$ between 0.2 and 111. The comparison of dimensionless shock-off distance $\tilde{\Delta}$ between present numerical results and Wen & Hornung's theory is shown in

Fig. 4. It is clearly demonstrated that the present code is accurate throughout the whole non-equilibrium flow regime. The largest difference between numerical method and the theory is about 6.7% which occurs at medium $\tilde{\Omega}$ value. Notably, the numerical shock stand-off distance is a little larger than that of Wen & Hornung's theory. It is because Wen & Hornung used a piecewise linear function to describe the density distribution on the stagnation line and the average density was slightly overestimated. Consequently, the shock stand-off distance is underestimated².

Figure 5 shows the density profiles and N atomic distributions of different sphere radii. When the freestream condition is fixed, the value of chemical reaction parameter $\tilde{\Omega}$ will increase with sphere radii per the definition of $\tilde{\Omega}$. It indicates that when the gas flows over a sphere, the gas has more time for dissociating and energy relaxation in the larger sphere cases and the dissociating level, i.e. the mass fraction of N atoms, is therefore higher. Meanwhile, the density behind the shock also reaches a higher level and the distribution of vibrational temperature is closer to that of translational temperature (See Fig. 6). For the case of $R=0.0025$ inch, the highest mass fraction of N only reaches to about 0.036, and the highest dimensionless density is just over 6 which is the density ratio of frozen flows. For the case of $R=40$ inches, the highest

mass fraction of N is higher than 0.2, and the highest dimensionless density approaches 9.8 which is the density ratio of fully equilibrium flows.

Figure 5. Distributions of dimensionless density (ρ/ρ_∞ , upper) and mass fraction of atomic nitrogen (lower) for nitrogen flows

Figure 6. Translational temperature (T , upper) and vibrational temperature (T_v , lower) for nitrogen flows.

C. Air Flows

Table 3. Freestream conditions of air flow cases selected from Wen & Hornung²

Case No.	R (inch)	ρ_∞ (kg/m ³)	u_∞ (m/s)	T_∞ (K)	Mass fraction of N ₂ , O ₂ , NO, N, O
5	0.5	0.0584	4110	1590	0.724, 0.180, 0.064, 2.39e-8, 0.0171
6	1	0.0278	3930	1370	0.724, 0.171, 0.065, 5.91e-9, 0.0262
7	1.5	0.03	3960	1410	0.724, 0.171, 0.0648, 8.33e-9, 0.0259
8	2	0.0158	5560	2620	0.743, 0.0341, 0.0252, 3.97e-5, 0.184

Table 4. Experimental, theoretical and numerical dimensionless shock stand-off distance, $\bar{\Delta}$, for air flow.

Case No.	Experiment (Wen & Hornung)	Theory (Wen & Hornung)	Simulation
5	0.101	0.092	0.092
6	0.105	0.093	0.095
7	0.103	0.093	0.093
8	0.09	0.084	0.087

Figure 7. Comparison of the numerical and experimental shapes of the bow shock for air flows.

Figure 8. Comparison of dimensionless shock stand-off distance for air flow

Air flow is much more complicated than nitrogen flow but is very important in practice. First, we also pick four air flow cases from Wen & Hornung's experiments. The freestream conditions and the dimensionless shock stand-off distance comparison are listed in table 3 and 4. Good agreement between experimental, theoretical and numerical results is observed. The numerical shapes of the entire bow shocks are also very close to the experimental results, as

shown in Fig. 7.

The freestream conditions of case 6 is adopted and the radii of spheres are varied to obtain different $\bar{\Omega}$ between 0.595 and 62.4. The comparison of numerical and theoretical dimensionless shock stand-off distances is shown by Fig. 8. The largest error is only about 6%. Figure 9 shows the distributions of N and O atoms. It is found that the mass fraction of O atoms is much higher than that of N atoms. It is because that the characteristic dissociating temperature of O_2 (59,500K) is much lower than that of N_2 (113,200K). Under the same temperature, the dissociating level of O_2 is much higher than that of N_2 . Even for the case of $R=40$ inches ($\bar{\Omega}=62.4$), the mass fraction of N is only about 0.6%, but the mass fraction of O reaches to 20%. On the upper side of the sphere, there is almost no N due to the flow expansion. The consequent significant temperature decrease during the flow expansion yield the full recombination of the atomic nitrogen. On the other hand, the mass fraction of O is still more than 10%. The distribution of translational temperature and vibrational temperature is similar with that of nitrogen flows (see Fig. 6).

(a) $\tilde{\Delta} = 1.26$ (b) $\tilde{\Delta} = 3.48$ (c) $\tilde{\Delta} = 10.4$ (d) $\tilde{\Delta} = 62.4$
Figure 9. Mass fraction of N_2 , N , O_2 , O and NO molecules for airflows

D. Carbon Dioxide Flows

Table 5. Freestream conditions of CO_2 flow cases selected from Wen & Hornung²

Case No.	R (inch)	ρ_∞ (kg/m ³)	u_∞ (m/s)	T_∞ (K)	Mass fraction of CO_2 , O_2 , CO , O , C
9	0.5	0.0584	4110	1590	0.724, 0.180, 0.064, 2.39e-8, 0.0171
10	1	0.0937	3100	1900	0.739, 0.0941, 0.166, 0.0008, 0.0001
11	1.5	0.150	2560	1240	0.922, 0.028, 0.049, 0.0005, 0.0005
12	2	0.0326	3490	2010	0.459, 0.185, 0.344, 0.0115, 0.0005

Table 6. Experimental, theoretical and numerical dimensionless shock stand-off distance, $\bar{\Delta}$, for CO_2 flow.

Case No.	Experiment (Wen & Hornung)	Theory (Wen & Hornung)	Simulation
9	0.101	0.092	0.092
10	0.0898	0.093	0.0876
11	0.090	0.093	0.0898
12	0.088	0.084	0.087

Figure 10. Comparison of the numerical and experimental shapes of the bow shock for CO₂ flows.

Figure 11. Comparison of dimensionless shock stand-off distance for CO₂ flow

To perform accurate modeling for reentry of space vehicles in the Martian atmosphere is of primordial importance to study reacting carbon dioxide flows, primary element in the Martian atmosphere. We selected four CO₂ flow cases from Wen & Hornung's experiments. The freestream conditions and the dimensionless shock stand-off distance comparison are listed in table 5 and 6. Fig. 10 shows the comparison of the bow shock shapes between the numerical analysis and the experimental

results. A good agreement is observed.

The freestream conditions of case 10 were adopted and the radii of spheres are varied to obtain different between 1.539 and 50.5824. The comparison of numerical and theoretical dimensionless shock stand-off distances is shown on Fig. 11. The largest error is about 5.05%. Figure 12 shows the distributions of CO₂ and O atoms.

(a) $\bar{\Omega} = 1.26$ (b) $\bar{\Omega} = 3.48$ (c) $\bar{\Omega} = 10.4$ (d) $\bar{\Omega} = 62.4$
Figure 12. Mass fraction of CO₂ molecules (upper) and O₂ molecules (lower) for CO₂ flows

E. Heat flux

An Air flow case from Wen² experiments was selected to test the code capabilities regarding real gas effects. The free-stream conditions and free-stream mass are listed in table 7.

Table 7. Freestream conditions of Air flow case selected from Wen & Hornung²

Case No.	R (m)	ρ_∞ (kg/m ³)	u_∞ (m/s)	T_∞ (K)	Mass fraction of N ₂ , O ₂ , NO, N, O
13	0.038	0.0172	5250	2320	0.739, 0.0615, 0.0355, 1.04e-5, 0.151

The temperature profile along the stagnation streamline for the two-temperature model case can be seen in Fig. 13. The transfer of energy from initial kinetic energy into various degrees of freedom determines this. Translational and rotational equilibrium occurs very rapidly, giving a high translational temperature immediately across the shock as all the directed energy of motion is transformed into translational and rotational energy. Transfer into vibrational excitation takes longer and leads to a lower temperature as the energy is distributed among more degrees of freedom. Dissociation and electronic excitation take longer still, giving yet a further reduction in kinetic temperature, yielding the final equilibrium temperature.

Fig. 14 shows a comparison of surface heating between the present results, against Lee's theory, Wen's simulations and experiments². It can be observed that the heat transfer along the wall is accurately predicted using the CE/SE method, matching those results of Lee and Wen.

Figure 13. Temperatures profile along the stagnation streamline.

Figure 14. Comparison of surface heating against Lee's theory, Wen's simulations and experiments.

F. Validation of CVCV model.

An Air flow case from Knab¹⁴ experiments was selected to test the code capabilities regarding the coupled CV-CV model multiple vibrational temperature effects. A sphere of 0.1 m in diameter is tested under a Mach 12.7 flow. The freestream conditions are; a density of $1.6 \times 10^3 \text{ kg/m}^3$, and a temperature of 196 K. The initial mass fractions are $N_2=0.7718$, $O_2=0.183343$, $O=0.039827$ and $NO=0.00503$ where atomic nitrogen is negligible. The wall temperature is assumed to be fixed at 300 K.

Figure 15 shows a comparison of translational and vibrational temperatures along the stagnation streamline. As can be seen, behind the shock, vibrational energy modes become excited by the dominant translational-vibrational energy exchange. O_2 dissociation begins and vibrational energy removal keeps the vibrational temperature of O_2 from overshooting the translational temperature.

We can observe that the vibrational temperature of NO is over predicted near the wall, this is an effect of the non-equilibrium modelling of the exchange reactions, where nitric oxide is formed in the reverse direction of the exchange reaction $NO + O \rightleftharpoons O_2 + N$, but also destroyed in the reverse direction in $N_2 + O \rightleftharpoons NO + N$. The CV-CV model predicts the average vibrational energy gain in an endothermic exchange reaction to be greater than the average vibrational energy loss in an exothermic exchange reaction, therefore we get a positive coupling term for NO leading to an increase in the vibrational temperature of nitric oxide. Despite the over prediction near the wall that can be explained due to the different chemical model reaction rate parameters used in the current CE/SE code, the trend is similar to the one of Knab¹⁴.

Figure 15. Comparison of translational and vibrational temperatures along the stagnation streamline of the 0.1m sphere against Knab's simulations¹⁴.

CONCLUSIONS

A CE/SE code based on hybrid meshes is extended to study the hypersonic non-equilibrium flows. The code is proved capable of simulating hypersonic flows accurately by comparing the numerical shock stand-off distances and bow shock shapes with Wen & Hornung's experimental results and theoretical model, the code also shows good accuracy in simulating heat flux in air flows around spheres.

Moreover, the influence of $\tilde{\Omega}$ on the flow features is studied in detail. The results show that the flow features are very sensitive to the value of $\tilde{\Omega}$. When $\tilde{\Omega}$ increases, there is more time for the dissociation of gas molecules and energy relaxation when the flow passes the sphere. Thus, both the density and the vibrational temperature will increase, and the bow shock will be "closer" (dimensionless shock stand-off distance is smaller) to the body. Although air flows are much more complicated than nitrogen flows, but the flow features are also mainly controlled by the dimensionless reaction rate parameter, $\tilde{\Omega}$. Therefore, $\tilde{\Omega}$ can be considered as a dominant dimensionless parameter in non-equilibrium flows.

Simulations were performed to calculate the heat transfer and compare the different gas models implemented, two temperature model and CV-CV. The code is proved capable of capturing the numerical shock standoff distances and bow shock shapes with Wen & Hornung's experimental results and Knab et al. numerical model. Moreover, the code shows good accuracy in simulating heat flux in air flows around spheres.

To improve the code capabilities regarding real gas simulations, the future work will be focused on the inclusion of different models for thermo-chemical non-equilibrium such as those by Liu et al.³² and Munafò et al.³³.

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