Coupled heat transfer characteristics on gas-solid reacting interface in carbon-oxygen dissociating environment for spacecraft entry flow

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Received: 9 December 2019; Revised: 14 February 2020; Accepted: 1 April 2020

Abstract
High-enthalpy dissociating aerodynamic environment during high-speed spacecraft entries brings new challenges to the prediction of heat transfer characteristics on the surface of thermal protection system. This study numerically dealt with the coupling modeling of chemically reacting interface in carbon-oxygen dissociating environment in order to accurately and reliably predict the Mars entry heating load. Computational fluid dynamics, computational heat transfer and interface balance with proper coupling strategy were involved in the coupling algorithm to take into account the surface catalysis, material ablation and structural thermal response. Numerical simulation shows that the interfacial reaction model has influences on coupling evolution by exchanging various patterns of heat transfer on the interface, including that from temperature gradient, that caused by chemical reaction, and that carried by the injection kinetic energy. The types and energy barriers of interfacial reaction were found to change the aerodynamic heating enhancement and its evolution over coupling time, which is the most remarkable difference from the perfect gas result. Gas-solid interaction involving interfacial reaction exhibits three distinct temporal intervals: the initial, developing and fully developed stages, and the chemical dynamics and heat transfer characteristics vary at different temporal scales. Related research provides important technical support for the design of thermal protection system for space vehicles.

Keywords: Heat transfer, Reacting flow, Numerical simulation, Hypersonic, Carbon-oxygen dissociation, Coupling, Surface catalysis, Material ablation

1. Introduction

Planetary spacecrafts, such as return capsules and Mars entry vehicles, enter the atmosphere at extremely high speeds, and therefore high-enthalpy dissociated aerodynamic environment occurs around the heat shield (Gnoffo, 1999). Such severe environment brings complex interface heat transfer processes between the gas and solid domains. Moreover, deep space exploration, such as hypersonic Mars entry mission, causes an additional carbon-oxygen (C-O) reacting environment, which further brings some new challenges to the evaluation of interface heat transfer characteristics (Reynier, 2014).

Accurate and reliable prediction of interface heat transfer is the premise and basis for effectively ensuring the safety of the spacecraft thermal protection system (TPS), reducing design redundancy and increasing the effective payload (Duffa, 2013). With the continuous and in-depth development of high-performance computing, using the numerical technology to characterize fluid mechanics, structural heat transfer, interface chemistry and their interaction has become an effective way to solve this problem (Milos and Rasky, 1994).

Early researches on interface heat transfer characteristics were done by solving the compressible gas dynamics equations with simple mathematical closure on the solid surface (Wright, et al., 2010). No interface chemistry was the
simplest and the most easily considered approach to model the surface, which generates the lowest energy exchange rate from the perspective of catalysis. The infinitely fast chemical reaction on the interface gives the other extreme of energy exchange, which is typically called fully catalytic wall. These two extremes are usually non-physical, and the actual interface is at finite-rate chemistry state with moderate energy exchange rate.

For non-ablative TPS, the influences of interfacial reaction coefficients on aerodynamic heating rely largely on the TPS material serving as the catalyst. For the C-O dissociated aerodynamic environment, a single-step catalytic model involving the basic recombination reactions of O2 and CO2 was developed (Bose et al., 2006). On this basis, the aerodynamic heating level and the corresponding uncertainty were obtained for Mars entries. The above model did not consider the route details of chemisorption and recombination. Thence, a two-step catalytic model with chemisorption and recombination rates controlled was proposed by Mitcheltree and Gnoffo (1995). The C-O chemistry includes recombination of gaseous and adsorbed atoms/molecules obeying the Eley-Rideal mechanism. The convective heating considering catalytic effects was obtained and the ratio is consistent with Viking flight data.

When the TPS material is sufficiently active to participate in interfacial reaction, mass-injecting ablation occurs on the gas-solid interface. A specific ablating boundary condition was established to numerically simulate the graphite oxidation and sublimation by Keenan and Candler (1993, 1994). To take into account the weak ablation effect of carbon-phenolic heatshield, a finite-rate carbon oxidation with complex boundary conditions was further defined by Chen and Milos (2004). Facing complex chemical reactions on the gas-solid interface, the chemical reaction pathways and the corresponding coefficients are unknowns. The determination of them is problematic and needs to be obtained according to experimental data or microscopic simulation (Herdrich et al., 2012).

In order to more accurately evaluate the heat transfer characteristics, the behavior inside the TPS structure should also be considered, because the structure temperature distribution affects the flow characteristics. Coupling study of computational fluid dynamics (CFD) and computational heat transfer (CHT) provides a good approach to solve the above problem (Mo et al., 2015). It has been studied for years focusing on hypersonic perfect air flow around spacecraft TPS structure (Thornton and Dechaumphai, 1988, Dechaumphai et al., 1989). On this basis, a coupling algorithm between chemical reacting flow and solid heat transfer in the C-O reacting system was further established by Chen, et al. (1995), and the thermal evaluation problem of Mars entries was firstly solved by means of coupling simulation. In order to effectively design the TPS structure and thickness, the integrated energy exchange was also dealt with by performing coupling simulation (Milos et al., 1999).

Future higher speed spacecrafts, especially next generation Mars entry vehicles, will faces higher enthalpy aerodynamic environment and more complex interface chemistry phenomenon. The heat transfer evaluation covers the simulation of both multi-physical coupling and interface chemistry. This problem is of critical importance for design and optimization of future spacecraft TPS. The traditional simulations were performed either with perfect-gas based multi-physical coupling method taking no interface chemistry into account, or using chemical boundary conditions without any thermal response of TPS materials. Occasionally, a combined solution was obtained, but it rarely contains three-dimensional or multi-action driven interface model (Wright, 2007).

The objective of this article is to characterize the heat transfer characteristics in the C-O dissociated aerodynamic environment using the three-dimensional coupling numerical techniques. Based on this method, the effects of various factors related to aerodynamics on the interface heat transfer characteristics were quantitatively analyzed. The heat transfer behaviors and characteristics were further discussed from the perspective of multiple temporal scales. Related researches provide important technical support for the TPS design of future spacecrafts for next generation Mars entry and return mission.

2. Method and Algorithm

2.1 CFD technique for gas flow

It is well known that the CFD technique is currently the most widely used tool for the solution of convective heat transfer (Ferziger and Peric, 2012). CFD considers the gas that follows the three laws of conservation, that is, the conservation of mass, momentum and energy, which are the well-known Navier-Stokes (NS) equations. When the flow speed is extremely high, the post-shock gas reacts and the high-enthalpy non-equilibrium flow generates. The conservation of mass turns into multiple species continuity equations with chemically reacting source terms (Cheng and Emanuel, 1995). See Appendix A for detailed description of controlling equations.
The solver employs the finite volume method based on three-dimensional structured grids. The code runs with Van Leer flux-vector splitting method to compute inviscid fluxes with total variation diminishing (TVD) limiter (Yee et al., 1985) and MUSCL variable extrapolation (Van Leer, 1979). The lower and upper symmetrical Gauss-Seidel (LUSGS) algorithm is used for time marching (Yoon and Jameson, 1987). The local integration algorithm is used for sub-iteration of the chemical source terms to avoid the matrix inversion in the LUSGS algorithm.

### 2.2 Computational structural heat transfer

Computational techniques for simulating heat transfer in complex system have reached maturity. The transient thermal response in the solid-phase TPS obeys the law of conservation of energy and is then characterized by the three-dimensional heat conduction equation. Taking temperature as the primary variable, the differential form of heat conduction equation is

$$\rho c_p \frac{\partial T}{\partial t} = \nabla \cdot q^T + \Omega$$  \hspace{1cm} (1)

where the parameters describing the thermal properties are functions of the local temperature. Recession due to oxidation is assumed to be small and thus the resulting mass loss of TPS can be ignored.

The solver for CHT uses the finite volume method based on the structured, unstructured and hybrid grids. The spatial discretization uses the second order central scheme, while the transient evolution uses the second order TVD Runge-Kutta method (Gottlieb and Shu, 1998).

### 2.3 Interface balance modeling with chemistry

In hypersonic non-equilibrium flow, the impingement of the gaseous particles on the solid-phase TPS brings gas-solid interaction and interface heat transfer behavior. The controlling equations on the gas-solid interface also obey the laws of conservation of mass, momentum and energy. However, compared with the fluid dynamics equations, the laws of conservation are locally reduced to interface balance (IB) equations (Milos and Rasky, 1994), and for the steady state we have

$$\sum_{\text{species}} (J - \rho Y^T u) \cdot n = J_{wn}$$  \hspace{1cm} (2)

$$\nabla p \cdot n = 0$$  \hspace{1cm} (3)

$$\left( q^f + h \cdot J \right) \cdot n = q^s + q_w^r$$  \hspace{1cm} (4)

where \( n \) is the identity vector normal to gas-solid interface, and \( J_{wn} \) is a set of the net mass fluxes for all the \( N \) species on the interface. For the interface heat transfer terms, \( q^f \) is the heat flux vector from temperature gradient, and \( h \cdot J \) is that from surface chemical reactions, \( q^s \) is the in-depth heat flux transferring into the thermal protection structure, and \( q_w^r \) is the thermal load radiated from wall to the far field with background temperature.

On the gas-solid interface, all the quantities but the net mass flux can be solved from or can be provided for CFD and CHT processes. The net mass flux \( J_{wn} \) is determined by interfacial reaction, the rate of which depends on chemistry mechanism. Taking into consideration the multi-species and multi-reaction system on the gas-solid interface, one given species can participate in one reaction pathway or several, possibly serving as the reactant or product. Considering both forward and backward processes, we have the net molar flux on the interface for species \( s \)

$$I_{wn,s} = \sum_{c=1}^{N_c} (v_{sc}^* - v_{sc}^r) I_c$$  \hspace{1cm} (5)

where \( N_c \) is the number of reaction pathways, and \( v^r (v^s) \) is the stoichiometric coefficient of reactant (product). The molar flux in pathway \( r \), where species \( s \) participates as the product \( (v^s > 0) \), contributes to the total mole flux, while the flux
for species $s$ as the reactant ($\nu' > 0$) must be subtracted from the total mole flux. Thus, the molar production or loss of any species on the interface is the summation of the individual production from each reaction.

The mole flux of specified reaction pathway is dependent on the species molar concentration and reaction rate coefficients as (Josyula, 2015)

$$I = k_f \prod_{i=1}^{N_r} X_i^{\nu_i'} - k_b \prod_{i=1}^{N_i} X_i^{\nu_i''}$$

(6)

where $N_r$ is the number of species in a given reaction process, $X$ is the species molar concentration, and $k_f$ ($k_b$) is the forward (backward) reaction rate coefficient. The value of these rate coefficients must be specified for each interfacial reaction, which needs the details of surface chemistry mechanism.

The high-enthalpy dissociated gas interacts with the TPS materials in various forms of chemical reactions, typically such as surface catalysis and ablation. Surface catalytic reactions produce huge heat transfer on the gas-solid interface though there is no net mass exchange between the impinging gas and the heat shield structure. However, surface ablating reactions generate additional net mass exchange, due to mass injection from thermal protection materials. The surface catalysis can account for different reactions such as the particle adsorption/desorption, the recombination of the gaseous atom with an atom adsorbed on the wall (Eley-Rideal mechanism), or the recombination of two adsorbed atoms (Langmuir-Hinshelwood mechanism) (Herdrich et al., 2012). The surface chemistry also involves the bulk carbon participating reactions since weak ablation is considered.

The rate coefficients for the surface reactions are obtained from kinetic theory, and are of the following form (Marschall and MacLean, 2011)

$$k_f = \gamma \frac{\bar{V}}{4\Phi_s} T^{\nu_0} \exp \left( \frac{E_s}{R_0 T} \right)$$

(7)

where the reaction probability $\gamma$ refers to catalytic/ablating efficiency or sticking coefficient, $\Phi$ is the total density of adsorption sites and the energy barrier $E$ describes the Arrhenius-type dependence of interface chemistry on temperature. The mean thermal speed of atoms/molecules concerned is related with the local temperature as

$$\bar{V} = \sqrt{\frac{8K_\text{B}T}{\pi M}}$$

(8)

These surface reactions are assumed to be irreversible and the reaction rates rely on the reactant concentration. Since it is difficult to quantify the adsorption dynamics, we define the effective catalytic/ablating efficiency or sticking coefficient by integrating the original $\gamma$ and the recombination/sticking ratio

$$\bar{\gamma} = \gamma \frac{X_s^{\nu_s'}}{\Phi_s^{\nu_s'}}$$

(9)

By definition we have

$$0 \leq \bar{\gamma} \leq \gamma \leq 1$$

(10)

Through parametric simulation studies, we can obtain catalytic/ablating heating performance of thermal protection materials.

2.4 Coupling procedure

Coupling analysis of multi-physical fields concerned should be employed so as to recognize the details of heat
transfer on the gas-solid interface. Physically and spatially, the whole system is decomposed into three modules: CFD, CHT and IB (Hirschel and Weiland, 2009). The coupling model is established by connecting these three computational modules with proper coupling strategy. The relation of these three physical fields and their inter-field data transfer is presented in Fig. 1.

![Relation of three physical fields (CFD, CHT and IB) and inter-field data transfer. CFD provide a) the mass flux $Y$, b) the heat transfer driven by temperature gradient $q^i$, and c) that by mass fraction $h \cdot J$ for IB. IB backwards provide a) the interface-normal speed $u$ due to mass injection for CFD, and further provide b) the heat flux $q^s$ at the structural side. For the module of CHT, the radiant energy transmission $q_w^r$ is taken into account for IB computation, and the temperature $T_w$ is obtained for the use of other modules concerned.](image1)

For the coupling computation, each partition is solved separately, and proper inter-field data transfer strategy should be implemented between these fields through spatial interpolation. For the details of coupling computation procedure, one can refer to Fig. 2. At the initial time or the individual time when the previous solution has already been all known, noting as $t_0$, the CHT module is processed for a time step of $\Delta t$, and as a result the new transient solution in the structure domain is obtained. Based on the newly obtained $T_w$, the IB is computed to update $u$. The CFD module is then steadily processed to obtain the interface quantities needed by the IB module. After updating the IB module, we obtain all the solution at the new time $t_0 + \Delta t$. Using the above data transfer sequence, the entire coupling simulation will progress smoothly.

![Procedure of coupling computation of CFD, CHT and IB. Process 0: data duplicating for re-run/updating; 1: transient CHT run; 2: new $T_w$ for CFD run; 3: new $T_w$ for IB updating; 4: new $u$ for CFD run; 5: new $q^i$, $h \cdot J$ and $Y$ for IB updating; 6: new $q^s$ for CHT run.](image2)

Variable coupling time step related with the stagnation heat flux was used to perform coupling simulation as...
\[ \Delta t_i = \Delta t_0 + k \left( q_0 - q_{i-1} \right) / \left( q_0 - q_{\text{re}} \right) \]  

(11)

where \( \Delta t \) denotes the time step, \( q \) denotes the stagnation heat flux, \( k \) is the slope to calculate time step increment, and the subscripts 0, re and \( i \) are variables at the initial time, at the radiation equilibrium state and at the current time.

### 2.5 Validation

The numerical algorithms were verified through the combination of two wind tunnel experiments, since it is difficult to employ an experiment to reproduce the actual physical phenomenon for the current complex system. The first experiment is a long-duration wind tunnel testing with hypersonic perfect-gas air flow (Dechaumphai et al., 1989, Wieting and Holden, 1989) to verify the gas-solid coupling procedure. One can see details in previous work (Yang et al., 2018). The second one is a high-enthalpy, chemically reacting testing with the desired testing gas in short-duration impulse facilities (MacLean et al., 2005). For detailed data, one can refer to the previous work (Yang et al., 2018b). The validation work demonstrates the feasibility of the current algorithms to deal with coupled heat transfer problem with interface chemistry.

### 3. Computational models for Mars entry

#### 3.1 Geometry model

The research object for coupling simulations is an axisymmetric Mars entry vehicle for ballistic entry (Braun and Manning, 2007). The vehicle is a blunt body of sphere-cone type with a semi-cone angle is 70 degrees. The back cone is not considered in the current simulation, because the aft-body flow generates relatively smaller aerodynamic force/heating and then has little impact on the upstream flow in front of the heat shield. Since the entry angle of attack is zero, a quarter of the gas-interface-structure domain is taken for computation. The thermal protection structure inside the heat shield involves multi-layer materials with uniform thickness. The heat transfer to the capsule cabin is neglected, because the amount is small (Milos et al., 1999). The detailed dimensions of the Mars Pathfinder geometry and thermal protection structure are shown in Fig. 3.

![Fig. 3 Detailed dimensions of Mars Pathfinder geometry and thermal protection structure.](image)

The detailed computational grids of the gas-interface-structure domain are described in Fig. 4.
were used to discretize the computation domains for the chemically reacting flow and heat transfer solvers. The grid in the gas domain is multi-block and structured, while in the solid domain it is unstructured. On the gas-solid interface, the grid is two-dimensional, quadrilateral and structured for IB updating. The grid in the thermal boundary layer is orthogonal and dense in the direction normal to wall so as to accommodate the great gradient of quantities concerned. Fine grid is also required in the solid domain near the interface to figure out the large gradient of temperature. In order to maintain high data transfer accuracy, the nodes of the IB grid exactly one-to-one corresponds to that of CFD/CHT grids on the surface boundary. By this means, the data errors caused by spatial interpolation techniques will be eliminated. After a serial of grid refinement studies (Yang et al., 2018b), the grids listed in Table 1 in have all been tested to be grid-independent for CFD/CHT computations and IB updating.

![Fig. 4 Detailed computational grid of the gas and solid domains and the gas-solid interface. CFD: Multi-block hexahedral structured grid; CHT: Hexahedral un-structured grid; IB: Multi-block two-dimensional quadrilateral structured grid.](image1)

Table 1 Details of computational grids for CFD/CHT computation and IB updating.

| Region          | Gas domain | Gas-solid interface | Solid domain |
|-----------------|------------|---------------------|--------------|
| Computation module | CFD | IB | CHT |
| Type of grid     | Structured | Structured | Un-structured |
| Type of cell     | Hexahedral | Quadrilateral | Hexahedral   |
| Cell number      | 46 592   | 832     | 36 096      |
| Node number      | 78 000   | 1 300   | 51 129      |

3.2 Reaction models
3.2.1 Gaseous reaction model

Reasonable gas and material models are essential for accurate prediction of heat transfer in the C-O dissociated aerodynamic environment for spacecraft entries. For the Mars entry gaseous flow, the gas is assumed to completely carbon dioxide (CO₂). In severe aerodynamic environment, the gas chemically reacts to form other species, such as CO, O₂, O and C, and further the reactions are in chemical non-equilibrium state.

For CO₂ dissociation issue, 18 reversible chemical reactions are involved in the gas domain. For details one can refer to Appendix B. The coefficients of reaction rate are from Park et al. (1994). The heat of formation ΔH₀ for candidate gaseous species is listed in Table 2. For a specified reaction, the heat release or loss is the difference of heat of formation between the products and reactants.
polynomial fitting is used to approximately express the functions of temperature. Though specific heat at constant pressure and conductivity of the outermost protection structure is conduction. The parameters of thermal properties are listed in Table 2.

### 3.2.2 Interfacial reaction model

The chemical reactions on the gas-solid interface are reduced to the two-dimensional reactions, where the chemical adsorption sites and bulk species (such as carbon atoms) participate. For interface catalysis, the reactions of gaseous oxygen atoms and carbon monoxide molecules adsorbed on the chemical adsorption sites are involved as (Mitcheltree and Gnoffo, 1995)

\[
\begin{align*}
O + (s) & \rightarrow O(s) \\
CO + (s) & \rightarrow CO(s)
\end{align*}
\]

where \( (s) \) is the empty adsorption site, while \( O(s) \) or \( CO(s) \) denotes the occupied adsorption site. For the molecules desorbed from these sites, the desorption reactions of oxygen and carbon dioxide are inversely involved as

\[
\begin{align*}
O_2(s) & \rightarrow O_2 + (s) \\
CO_2(s) & \rightarrow CO_2 + (s)
\end{align*}
\]

Based on the species on the adsorption sites, the gaseous species combines with the adsorbed species, following the Eley-Rideal mechanism. To model the catalysis of molecular oxygen and carbon dioxide, three recombination reactions are considered (Mitcheltree and Gnoffo, 1995)

\[
\begin{align*}
O + O(s) & \rightarrow O_2(s) \\
CO + O(s) & \rightarrow CO_2(s) \\
O + CO(s) & \rightarrow CO_2(s)
\end{align*}
\]

Through various reactions of adsorption (R 1, R 2), desorption (R 3, R 4) and recombination (R 5 ~ R 7), three catalytic pathways form: ER1 (R 1 + R 5 + R 3), ER2 (R 1 + R 6 + R 4), and ER3 (R 2 + R 7 + R 4). Pathways ER2 and ER3 produce 528 kJ/mol of heat, respectively, while ER1 does 498 kJ/mol.

For interface ablation, the gaseous oxygen atoms/molecules combine with the solid-phase carbon atoms on the surface of the thermal protection material. Two types of combination, Ox1 (R 8) and Ox2 (R 9), are involved as (Keenan and Candler, 1994)

\[
\begin{align*}
O + C(b) & \rightarrow CO + (b) \\
O_2 + C(b) & \rightarrow CO + O + (b)
\end{align*}
\]

where \( (b) \) denotes the bulk atom. Oxidation R 8 is exothermic reaction, producing 363 kJ/mol of heat, while R 9 is endothermic, absorbing 135 kJ/mol.

### 3.3 Thermal properties of gases and materials

Due to the sharp increase of internal energy across shock wave, the vibrational energy of diatomic and triatomic molecules will be excited to some degree, and the internal energy further increases. Table 2 lists the detailed data (molecular/atomic weight \( M \), vibrational temperature \( T_{vib} \) and degeneracy \( g \)) of the excitation of vibrational energy for candidate gaseous species. Such excitation is conventionally instantaneous and the relaxation time is assumed to be zero. So, the flow is in vibrational equilibrium state (Suzuki and Abe, 1994).

Apart from a small amount of reactions occurring on the surface, the typical heat transfer pattern in the thermal protection structure is conduction. The parameters of thermal properties are listed in Table 3 (Milos et al., 1999). The specific heat at constant pressure and conductivity of the outermost SLA-561V vary with temperature, and quadratic polynomial fitting is used to approximately express the functions of temperature. Though the thermal properties of

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Table 2 Thermochromical data of candidate gaseous species.

| Index | Species | \( M \) [kg/kmol] | \( T_{vib} \) [K] | \( g \) | \( \Delta H_0 \) [J/kmol] |
|-------|---------|------------------|----------------|-------|------------------|
| 1     | CO\(_2\) | 44               | 945            | 2     | -3.9×10⁸         |
| 2     | CO      | 28               | 3122           | 1     | 1.1×10⁹          |
| 3     | O\(_2\) | 32               | 2239           | 1     | 0.0              |
| 4     | O       | 16               | -              | -     | 2.4×10⁹          |
| 5     | C       | 12               | -              | -     | 7.1×10⁹          |
A series of numerical simulations with various interface models, including the non-, fully and finite-rate catalytic/ablating walls, were performed using the newly established algorithms and models. Table 4 presents the details of interface conditions for coupling computation. The coupling simulation with non-reacting perfect-gas model (CPG) was also performed and then compared with the chemically reacting cases.

The flight speed is $V_\infty = 4862$ m/s at 28.5 km in height from the surface of Mars where the atmospheric temperature and pressure are $T_\infty = 173$ K and $p_\infty = 27.4$ Pa. Plasma was not considered, since it is weak for the current simulation condition and its influence on aerodynamic heating is limited. Through the coupled numerical simulations, the hypersonic flow field and structural temperature field were obtained, and the interface heat flux evolution was also given afterwards.

The initial temperature in the structure is set to be overall 300 K. For given temperature of 300 K on the gas-solid interface, the initial hypersonic flow field and interface balance state were therefore obtained. For the current simulation, the initial time step is $\Delta t = 1 \times 10^{-5}$ s, and the slope is set to be $k = 0.02$ s.

4. Coupling results
4.1 Energy transport properties

In order to manifest the energy transport properties induced by interface chemistry, the energy distribution was extracted from the simulation data. The energy distribution of various forms in hypersonic C-O flow field is shown in Fig. 5, including the static enthalpy, static internal energy, kinetic energy and dissociating energy. The free stream kinetic energy is typically converted into internal energy (enthalpy) across the bow shock wave. High internal energy increases the possibility of molecular vibration and chemical reaction in the shock layer. Therefore, a large degree of excitation of molecular vibrational energy and further dissociation occur in the shock layer. Internal energy exists mainly in the form of molecular vibration and dissociation. Molecular vibration and chemical bond cleavage in the shock layer largely decrease the local temperature compared with calorically perfect gas model. Due to chemical reaction, part of internal energy is shared by or transferred to dissociating energy, as is shown in Fig. 6 in detail. The dissociating energy decreases in the near-wall region because the atoms or small molecules chemically recombine on the wall.

### Table 3 Thermal properties of the thermal protection structure.

| Material               | $h$ [mm] | $\rho$ [kg/m$^3$] | $C_v$* [J/(kg⋅K)] | $\kappa$* [W/(m⋅K)] |
|------------------------|----------|-------------------|-------------------|---------------------|
| SLA-561V               | 19.95    | 232.26            | $-5.026 \times 10^4$ | $1.741 \times 10^5$ |
|                        |          |                   | 2.940 $\times 10^{-2}$ | 1.475 $\times 10^{-1}$ |
| Aluminum honeycomb     | 31.75    | 250.00            |                  |                     |
|                        |          |                   | 1200              | 0.022               |
| Polyimide faceplate    | 0.38     | 1380.00           |                  |                     |
|                        |          |                   | 1100              | 0.100               |

*Note: Quadratic polynomial fitting $y = aT^2 + bT + c$, $T$ in [K], data from (Milos et al., 1999).

### Table 4 Details of interface conditions for coupling computation (involved for √, otherwise for ×).

| Code     | Reacting gas | ER1   | ER2   | ER3   | Ox1  | Ox2  |
|----------|--------------|-------|-------|-------|------|------|
| CPG      | ×            | ×     | ×     | ×     | ×    | ×    |
| NCW      | ×            |       | ×     | ×     | ×    | ×    |
| FCW      | ×            | √     |       |       | ×    | ×    |
| Ca       | √            | √     |       |       | ×    | ×    |
| Ab1      | √            | ×     | ×     | ×     |      | ×    |
| Ab2      | √            | ×     | ×     | ×     |      |      |
| Ca+Ab2   | √            | √     |       |       | ×    |      |

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4.2 Coupling evolutions

For the coupling process of hypersonic flow with fixed free stream condition, the interface heat transfer rate typically decreases over the coupling time, from the initial higher heat flux to the final quasi-radiation-equilibrium one. Taking the result for FCW at $t = 5$ s as example, Fig. 7 shows the temperature distribution in the hypersonic non-equilibrium flow field and the velocity profiles in the boundary layer at three typical points. At the near nose point, the near-wall temperature is relatively high due to the stagnation effect, while it is low near the shoulder. The velocity near the stagnation point is smaller than other regions, because the kinetic energy is converted into internal energy across the shock. In order to distinguish the details of boundary layer during the coupling process, Fig. 8 presents the evolution of velocity magnitude and temperature near the gas-solid interface at the bottom point in Fig. 7. One can observe from figure that the temperature in the boundary layer and the solid domain increases with the coupling time, resulting in aerodynamic heating on the TPS. Meanwhile, the velocity magnitude (streamwise speed) drops slightly at a certain distance from the gas-solid interface (still in the boundary layer). The main reason is that the total energy is shared more by internal energy in the boundary layer with the rise of local temperature.
Fig. 7 Temperature contour in hypersonic non-equilibrium flow field and velocity profiles in the boundary layer at three typical gas-solid points. The computational condition is fully catalytic (FCW) on the gas-solid interface at the coupling time of 5 s.

Fig. 8 Evolution of velocity magnitude and temperature near the gas-solid interface during the coupling process. The moment $t = 1 \times 10^{-5}$ s can be seen as the initial state of the coupling process, while $t = 5$ s is near to the radiation equilibrium state.

Considering the coupling process with different interface chemistry mechanism, simulation results with various interfacial reaction models were compared at the initial (Initial bound) and quasi-equilibrium (Quasi-eq bound) stages in Fig. 9. In terms of interface catalytic characteristics, the initial and quasi-equilibrium heat fluxes on the non- (NCW), fully (FCW) and finite-rate (Ca) catalytic walls were compared. As the surface catalytic activity increases, the coupling heating increases correspondingly, and as a result NCW and FCW give two limits of the coupling thermal effect. In terms of interface ablating characteristics, the initial and quasi-equilibrium heat fluxes on the finite-rate ablating wall were also compared. The interaction between interface ablating and catalytic reactions exhibits a more complex coupling thermal effect.
Fig. 9 Interface heat fluxes with different interface conditions at the initial and quasi-equilibrium stages of the coupling process. NCW: no chemistry on the gas-solid interface; FCW: infinitely fast chemical reaction on the interface; Ca: Interface catalytic reaction including ER1, ER2 and ER3; Ab1: Interface ablating reaction including Ox1; Ab2: Interface ablating reaction including Ox2; Ca+Ab2: Interface composite reaction including catalysis ER1, ER2, ER3 and oxidation Ox2.

From Fig. 10 one can observe the dissociating energy with various gas properties and interface conditions. As is discussed above, the dissociating energy is important throughout the thin shock layer, until the gas encounters the gas-solid interface, where the atoms or small molecules recombine to form large molecules. From the figure we can see that the near-wall dissociating energy loss depends on interface models. If the material is modeled as a completely inert wall (not participating as a reactant in interface chemistry and non-catalytic to gaseous recombination), there is nearly no dissociating energy loss near the wall. If the material is an ideal active catalyst, the dissociating energy can be quickly reduced to zero due to the infinitely fast catalytic recombination. The finite-rate interfacial reaction (Ca) exhibits a medium dissociating energy loss. The coupling process with perfect gas was also simulated. One can also observe from Fig. 10 that no dissociating energy loss exists due to the completely inert gas property. The interface conditions nearly have no effect on the kinetic energy profile while the gas properties (chemically reacting or not) largely affect the kinetic energy distribution and the shock layer thickness. Due to the variety of energy forms, the space (shock layer) occupied by the blocked high-enthalpy compressible gas is more limited (thinner).

Fig. 10 Dissociating energy along the centerline with various gas properties and interface conditions. CPG: calorically perfect gas flow solver with no interface chemistry; NCW: no chemistry on the gas-solid interface; FCW: infinitely fast chemical reaction on the interface; Ca: Interface catalytic reaction including ER1, ER2 and ER3.
4.3 Influence of gas model on heat transfer characteristics

The gas model determines the energy conversion in the flow field and further affects the heat transfer characteristics on the interface. In order to evaluate such impact, coupling simulations based on calorically perfect gas (CPG) and chemical non-equilibrium gas model were performed.

The comparison of heat flux evolution for these two gas models was presented in Fig. 11. The heat flux generated from chemical non-equilibrium flow was found to be dispersed in a wide area due to undetermined interfacial reaction conditions. Such scatter is bounded by the non-catalytic wall (NCW) as the lower extreme and the fully catalytic wall (FCW) as the upper extreme. The finite-rate catalytic (Ca) result is located among the scatter. As to the CPG simulation, the coupling heat flux was also found to be located between the two extremes, generally close to the Ca value.

![Fig. 11 Comparison of heat flux evolution for calorically perfect gas and chemical non-equilibrium gas models.](image)

CPG: calorically perfect gas flow solver with no interface chemistry; NCW: no chemistry on the gas-solid interface; FCW: infinitely fast chemical reaction on the interface; Ca: Interface catalytic reaction including ER1, ER2 and ER3.

Although the result from CPG and Ca are similar, the energy conversion in hypersonic flow and wall heat transfer mechanism is quite different. The former undergoes neither chemical reactions nor the vibrational energy excitation. The thermodynamic parameters (such as specific heat) are independent on temperature. The latter experiences chemical reactions and the reactions are non-equilibrium. Meanwhile, the vibrational energy of gas molecules is excited with the rise of temperature. The former is dominated by temperature gradient in the boundary layer, while the latter is dominated by diffusion transport due to chemical recombination on the wall.

Taking the heat flux at the initial moment as the reference value, Fig. 12 presents the comparison of relative heat flux evolution for these two gas models. Since both NCW and CPG are inert on the wall, and both heat fluxes are derived from wall normal temperature gradient, the relative value drops similarly with the coupling time. Although the absolute values of heat flux from CPG and Ca are nearly the same, the relative values are quite different, because Ca has a large heat release during the initial stage of coupling process.

4.4 Influence of interface reaction on heat transfer characteristics

Numerical simulations with various interfacial reaction types and energy barriers were performed and the heat flux evolution was recorded to figure out the influence of interfacial reaction on heat transfer characteristics.

4.4.1 Interfacial reaction type

In Fig. 13, curves of coupled heat flux on the non- (NCW), fully (FCW) and finite-rate (Ca) catalytic walls with energy barrier $E_{ER}/R_0 = 1400$ K are compared. Generally, they follow a similar trend with the coupling time, and the
finite-rate heating lies between the NCW and FCW limits during the entire coupling process.

![Diagram 1](image1.png)

**Fig. 12** Comparison of relative heat flux evolution for calorically perfect gas and chemical non-equilibrium gas models. CPG: calorically perfect gas flow solver with no interface chemistry; NCW: no chemistry on the gas-solid interface; FCW: infinitely fast chemical reaction on the interface; Ca: Interface catalytic reaction including ER1, ER2 and ER3.

Two types of surface carbon-based material oxidation, the reaction involving atomic oxygen (Ox1) and that involving molecular oxygen (Ox2), were considered separately, and coupled heat fluxes from surface oxidation are compared in Fig. 14. Compared with the non-catalytic result, the heat flux with Ab1 was found to be higher than the NCW value via computation, because the combination of atomic oxygen with bulk carbon releases a certain amount of energy. The computed heat flux with Ab2, however, is lower than the NCW value. The reason for this opposite result is that the participation of molecular oxygen in the ablating reaction causes its chemical bond cleavage in the first step, consuming a large amount of energy.

Heat flux result of simulation with oxidation-participating (Ca+Ab2) catalytic condition was also presented in Fig. 13. Though Ab2 inhibits the energy release on the interface, the introduction of Ab2 to finite-rate catalytic reaction (Ca+Ab2) enhances interface heating level taking Ca as the reference. The reason for this phenomenon is that Ab2 consumes molecular oxygen and further promotes the catalysis of molecular oxygen recombination ER1.

![Diagram 2](image2.png)

**Fig. 13** Comparison of heat flux evolution for interface catalytic/abating reactions. NCW: no chemistry on the gas-solid interface; FCW: infinitely fast chemical reaction on the interface; Ca: Interface catalytic reaction including ER1, ER2 and ER3; Ca+Ab2: Interface composite reaction including catalysis ER1, ER2, ER3 and oxidation Ox1.
4.4.2 Interfacial reaction barrier

Energy barrier refers to the degree of chemical reaction difficulty at a specific temperature. The influence of Eley-Rideal energy barrier on heat transfer characteristics was numerically investigated by changing the adsorption/Eley-Rideal energy barriers $E_{Ad}$ and $E_{ER}$.

In Fig. 15 the catalytic heating evolution with various energy barriers was presented. The primary difference of finite-rate heating with different energy barriers occurs at the initial stage of the coupling process. When the energy barrier increases, higher energy is required to trigger surface recombination reactions. Therefore, the Eley-Rideal reaction gets difficult, and the chemical heat generation is reduced. Consequently, the stagnation heat flux at the initial stage is close to NCW result. With the development of coupling process, the heat shield gets aerodynamically heated and the wall temperature increases. The Eley-Rideal reaction becomes easier, especially for interface chemistry with higher energy barrier. As a result, heating augmentation from interface chemistry with higher energy barrier becomes remarkable at $t > 10^3$ s.

The influence of ablation energy barrier on heat transfer characteristics was also numerically investigated by changing
the energy barrier $E_{Ad}$ of Ab2. Note that the Eley-Rideal energy barrier is fixed to $E_{ER}/R_0 = 1400$ K. In Fig. 16, the influence of three different ablation energy barriers ($E_{Ab}/R_0 = 700$, 1400 and 2800 K) on stagnation coupled heat flux is shown under finite-rate ablation condition. One can observe that the ablation energy barrier acts with the same rule as the catalysis energy barrier.

![Graph showing heat flux evolution with various ablation energy barriers. FCW: infinitely fast chemical reaction on the interface; Ca: Interface catalytic reaction including ER1, ER2 and ER3 with $E_{ER}/R_0 = 1400$ K; Ca+Ab2: Interface composite reaction including all catalysis with $E_{ER}/R_0 = 1400$ K and oxidation Ox2 with $E_{Ab}/R_0 = 700$, 1400, 2800 K, respectively.]

5. Discussion

Based on the simulation results above, we discuss from the following two aspects: (1) how much influence interface chemistry introduces into aerodynamic heating; (2) the temporal scales of energy transport during the coupling process.

5.1 On heating composition introduced by interface chemistry

Considering the coupled heating process on the finite-rate chemical interface under the action of ablation, the proportion of the injecting and diffusing energy exchanges in the total heating level was analyzed. The various forms of coupled energy transfer rate involving single reaction Ab2 was shown in Fig. 17. It can be seen that, apart from the heat flux caused by temperature gradient and the diffusing energy exchange driven by interface chemistry, there is also a certain amount of heat transfer from the material injection. Under the current calculation condition, this additional heat transfer rate is an order of magnitude lower than the other two energy patterns. The ablating injection heating rate can be ignored for the current weak ablation. However, when the material ablating reaction gets strong, the ablating injection heating needs to be focused on.

5.2 On temporal scales of heat transfer

Gas-solid interaction involving interfacial reaction exhibits different dynamic behaviors and thermal characteristics at different temporal scales, which was investigated by analyzing flow and heat transport details near the interface.

From the temporal perspective, in different time intervals of coupling development, the interface heat transfer rate exhibits different evolutionary patterns, especially for interfacial reaction with higher energy barrier. Fig. 18 shows the evolution of interface heat transfer rate at finite-rate catalytic (Ca) and ablating (Ca+Ab2) walls with energy barrier $E_{a}/R_0 = 2800$ K. By the curve patterns, three time-scale intervals can be divided: the initial, developing and fully developed stages. The initial stage ($t < 0.02$ s, order of magnitude of millisecond) is a very short period of time after the onset of coupling process, where the interface chemistry dominates the heat transfer process. In the developing stage ($0.02$ s $< t < 1$ s), the interface chemistry and temperature gradient commonly control the heat transfer process. While when the coupling process continues ($t > 1$ s, order of magnitude of second), the decline of interface heat transfer rate decelerates.
and tends to the equilibrium state. Thereafter the heat transfer can be considered fully developed.

Fig. 17 Various patterns of coupled heat transfer rate under the action of ablation. Convection: heat flux driven by temperature gradient; Diffusion: heat flux driven by species mass fraction gradient caused by interfacial reaction; Injection: heat flux caused by mass injection due to material ablation.

Fig. 18 Interface heat transfer rate with finite-rate catalysis and ablation in different time intervals of coupling development. Ca: Interface catalytic reaction including ER1, ER2 and ER3; Ca+Ab2: Interface composite reaction including catalysis ER1, ER2, ER3 and oxidation Ox. Initial stage ($t < 0.02$ s): dominated by interface chemistry; Developing stage ($0.02$ s $< t < 1$ s): commonly controlled by interface chemistry and temperature gradient; Fully developed stage ($t > 1$ s): dominated by temperature gradient.

The correlation between interface temperature and heat flux under the coupling condition with linear curve fitting is presented in Fig. 19. With no or weakly temperature-dependent interface chemistry, the conventional heat transfer process over time is a continuous decline pattern. This correlation maintains high linearity (standard deviation $R^2 = 0.99932$) for the case without interface chemistry. The introduction of strongly temperature-dependent interface chemistry breaks the traditional evolutionary law. The linearity decreases slightly on the fully catalytic wall ($R^2 = 0.98198$). When the chemical activity on the interface is highly related to temperature, the linearity gets worse ($R^2 = 0.90975$).

To find out the reason why interface chemistry deteriorates the linearity of the above correlation, Fig. 20 divides the heat transfer rate into temperature-gradient and species-diffusion parts. One can observe that correlation for the species-diffusion part is much worse than the temperature-gradient part. Conventionally, the temperature increase causes the decrease of temperature gradient normal to wall, leading to a decrease of interface heat transfer rate. Since the chemical activity is highly dependent on temperature, the chemical energy release causes large enhancement of interface heat flux, which is
completely contrary to the conventional trend. In summary, the enhancement of chemical energy release accounts for this phenomenon.

![Graph](image1)

**Fig. 19** Correlation between interface temperature and heat flux under various interfacial reaction conditions. NCW: no chemistry on the gas-solid interface; FCW: infinitely fast chemical reaction on the interface; Ca: Interface catalytic reaction including ER1, ER2 and ER3. -fit: linear curve fitting.

![Graph](image2)

**Fig. 20** Correlation between interface temperature and heat flux from temperature-gradient and species-diffusion parts. Conv: heat flux component from temperature gradient; Diff: heat flux component from species mass fraction gradient due to interfacial reaction. -fit: linear curve fitting.

6. Conclusion

This paper dealt with coupled heat transfer characteristics on gas-solid reacting interface in C-O dissociating environment for spacecraft entries using interfacial reaction models and multi-disciplinary algorithms. Some conclusions can be drawn from the simulation results and in-depth discussion as follows.

(1) The interfacial reaction model has influences on coupling evolution by exchanging various patterns of heat transfer on the interface, including that from temperature gradient, that caused by chemical reaction, and that carried by the injection kinetic energy. The heat exchange is typically driven by species diffusion due to interfacial reaction.

(2) The types and energy barriers of interfacial reactions change the aerodynamic heating enhancement and the heat flux evolution over coupling time, which is the most remarkable difference from the perfect gas result.

(3) Gas-solid interaction involving interfacial reaction exhibits three distinct temporal intervals: the initial, developing and fully developed stages. The chemical dynamics and heat transfer characteristics vary at different temporal scales.
The current coupling method and procedure were well validated, and the simulation results are consistent with hypersonic entry physics. Consequently, the current conclusion renders research ideas for energy management and utilization for spacecraft TPS. Related research provides important technical support for the design of future spacecrafts.

Acknowledgment

The authors gratefully acknowledge the financial support of the National Natural Science Foundation of China through the projects No. 11702311 and 11702315. The work was also partially supported by the Postdoctoral Innovative Talent Support Program of China through the project No. BX20180371 and the National Key Research and Development Plan of China through the project No. 2019YFA0405202.

Appendix

A. Controlling equations for compressible reacting gas flow

The controlling equations for reacting gas flow are the compressible Navier-Stokes equations and in density-based conservation form can be written as

\[
\frac{\partial \mathbf{Q}}{\partial t} + \nabla \cdot (\mathbf{F}_c - \mathbf{F}_d) = \mathbf{S}.
\]

In this expression, the vector of conserved quantities is \( \mathbf{Q} = [\rho \mathbf{Y}, \rho \mathbf{u}, E_i]^T \), and the vector of source terms is \( \mathbf{S} = [\mathbf{\omega}, \mathbf{0}, \mathbf{0}]^T \). The convection and diffusion flux matrices are given by

\[
\mathbf{F}_c = \begin{bmatrix} \rho \mathbf{u}^T \mathbf{Y}^T \\ \rho \mathbf{u}^T + p \mathbf{I} \\ (E_i + p) \mathbf{u}^T \end{bmatrix} \quad \text{and} \quad \mathbf{F}_d = \begin{bmatrix} -\mathbf{J}^T \\ \tau \\ \mathbf{u} \cdot \tau - \mathbf{q}^T - (\mathbf{h} \cdot \mathbf{J})^T \end{bmatrix}.
\]

Note that we define \( \nabla = \left[ \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right] \) and \( \nabla \cdot \mathbf{J}^T = \left( \nabla \cdot \mathbf{J}^T \right)^T \). In the expressions above, \( \mathbf{u} = [u, v, w] \) represents the velocity components, \( \mathbf{Y} = [Y_1, Y_2, ..., Y_{N_s}] \), \( \mathbf{h} = [h_1, h_2, ..., h_{N_s}] \) and \( \mathbf{\omega} = [\omega_1, \omega_2, ..., \omega_{N_s}] \) represent the sets of the mass fraction, enthalpy and mass production rate for the \( N_s \) species, respectively, \( \tau \) is the stress tensor and \( \mathbf{I} \) is a \( 3 \times 3 \) identity matrix. The summation of all the species mass equations turn to be the global mass equation, and hence we have

\[
\sum_{s=1}^{N_s} Y_s = 1 \quad \text{and} \quad \sum_{s=1}^{N_s} \omega_s = 0.
\]

Each species is assumed to obey the equation of state for ideal gas, and the equation of state for the gaseous mixture therefore follows

\[
p = \rho T \sum_{s=1}^{N_s} \frac{Y_s}{M_s}.
\]

The directional heat flux vector driven by temperature gradient obeys the Fourier’s law with the following form

\[
\mathbf{q} = \kappa \nabla T.
\]

The matrix of directional mass flux for all the \( N_s \) species driven by species diffusion obeys the Fick’s law as

\[
\mathbf{J} = \begin{bmatrix} \rho D_{Y_1} \nabla Y_1 \\ \rho D_{Y_2} \nabla Y_2 \\ \vdots \\ \rho D_{Y_{N_s}} \nabla Y_{N_s} \end{bmatrix}.
\]
B. Chemical reaction equations

The chemical reaction equations for gaseous species in C-O reacting system used in hypersonic flow solver:

\[
\begin{align*}
2 \text{CO} & \leftrightarrow \text{CO}_2 + \text{C} \\
\text{CO} + \text{O} & \leftrightarrow \text{C} + \text{O}_2 \\
\text{CO}_2 + \text{CO} & \leftrightarrow 2 \text{CO} + \text{O} \\
\text{CO} + \text{C} & \leftrightarrow \text{C} + \text{O} + \text{CO}_2 \\
\text{CO}_2 + \text{C} & \leftrightarrow \text{CO} + \text{O} + \text{CO}_2 \\
\text{CO}_2 + \text{O} & \leftrightarrow \text{CO} + 2 \text{O} \\
\text{CO}_2 + \text{O} & \leftrightarrow \text{C} + \text{O} + \text{O}_2 \\
\text{CO}_2 + \text{O} & \leftrightarrow \text{CO} + \text{O} + \text{O}_2 \\
\text{CO}_2 + \text{O} & \leftrightarrow 2 \text{CO} + \text{O} + \text{O}_2 \\
\end{align*}
\]

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