Non-Equilibrium Distributions and Heat Transfer Near a Catalytic Surface of Re-Entering Bodies

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Abstract. Non-equilibrium vibrational-chemical kinetics and heat transfer in an O₂/O mixture near a silica surface are studied using the state-to-state approach. The effect of non-equilibrium kinetics and surface catalysis on the total heat flux and averaged dissociation rate coefficients is examined. The contribution of thermal conductivity, thermal and mass diffusion and vibrational energy diffusion to the heat transfer is evaluated.

INTRODUCTION

Thermal protection of hypersonic re-entry vehicles requires accurate models of heat transfer near a body surface taking into account real gas effects. The influence of non-equilibrium kinetics in the gas phase and on the surface of a hypersonic apparatus entering the Earth atmosphere on the total energy flux is the important problem of aerothermodynamics.

Recently we have considered this problem in the frame of the kinetic theory of gases in the state-to-state approximation [1, 2]. The state-to-state transport kinetic theory developed in [3] has been applied to the boundary layer problem [1]: the state-to-state vibrational distributions obtained in [4] have been inserted to the transport theory algorithms as input data for the heat transfer evaluation. The gas-surface interaction has also been described in the state-to-state approximation: for this purpose recombination to selected O₂ vibrational levels at a silica surface has been taken into account in [2] using the recombination mechanisms and rate coefficients proposed in [5, 6, 7].

In the next paper [8] this study has been extended to take into account a more realistic model for heterogeneous reactions at a silica surface. Recombination of oxygen atoms is permitted to any O₂ vibrational level [6, 7]. Also, the processes of O₂ dissociation and deactivation of its vibrational levels at the wall are taken into account. The aim of the present paper is to estimate the influence of these features on the transport properties in the O₂/O mixture. Besides that the effect of state-to-state distributions and mechanism of surface recombination on the gas phase dissociation rate has been considered, and essentially non-Arrhenius temperature dependence of rate coefficients has been found.

STATE-TO-STATE TRANSPORT PROPERTIES AND DISTRIBUTIONS

In this paper we consider the flow of O₂/O mixture with vibration-vibration (VV) and vibration-translation (VT) energy exchange, dissociation and recombination in the boundary layer, and focus the main attention on the dependence of the heat transfer and diffusion on the mechanism of non-equilibrium processes at the surface. Equilibration of the translational and rotational energies is assumed to proceed much more rapidly with respect to vibrational relaxation and dissociation-recombination processes which characteristic times are supposed to be comparable with the residence time of a particle in the boundary layer. The complete set of equations of a non-equilibrium flow follows from the kinetic equations and contains in this case the equations of detailed vibration-chemical kinetics for vibrational level populations of molecular species nᵢ, number density of atomic species nₒ and conservation equations of the momentum and total energy. These equations and corresponding transport terms are given in [3]. In the state-to-state approximation, the total energy flux is obtained as a sum of heat fluxes due to heat conductivity, thermal diffusion, mass diffusion of chemical species and also diffusion of vibrationally excited molecules [3]. The later process is described...
by the diffusion velocities of each vibrational state.

In the boundary layer approximation, after some simplifications, the following expressions for the total heat flux \( \boldsymbol{q} \), diffusion velocities of oxygen molecules at different vibrational levels \( \mathbf{V}_i \) and oxygen atoms \( \mathbf{V}_O \) can be written [2]:

\[
\mathbf{V}_i = - (D_n - D_{O_2-O_2}) \nabla (\frac{n_i}{n}) - D_{O_2-O_2} \nabla (\frac{n_{O_2}}{n}) - D_{T_0} \nabla \ln T
\]

(1)

\[
\mathbf{V}_O = - D_{O_2-O_2} \nabla (\frac{n_O}{n}) - D_{O_2-O_2} \nabla (\frac{n_{O_2}}{n}) - D_{T_0} \nabla \ln T
\]

(2)

\[
\boldsymbol{q} = - \lambda' \nabla T - p \left( D_{I_{O_2}} \nabla \frac{n_{O_2}}{n} + D_{I_O} \nabla \frac{n_O}{n} \right) + \sum_i \left( \frac{5}{2} kT + \langle \epsilon_{rot,i} \rangle + \epsilon_i \right) n_i \mathbf{V}_i + \left( \frac{5}{2} kT + \epsilon^O \right) n_O \mathbf{V}_O
\]

(3)

Here \( n \) is the total number density, \( p \) is the pressure, \( T \) is the gas temperature, \( k \) is the Boltzmann constant, \( \epsilon_i, \epsilon^O \) are the vibrational energy of a molecule and energy of oxygen atom formation, \( \langle \epsilon_{rot,i} \rangle \) is the averaged rotational energy, \( \lambda' \) is the thermal conductivity coefficient due to translational and rotational degrees of freedom, \( D_{ef} \) \((e = O_2, O)\) are the thermal diffusion coefficients, \( D_{ed} \) \((e, d = O_2, O)\) are the diffusion coefficients of different chemical species, \( D_{ii} \) are the self-diffusion coefficients of molecules at the vibrational level \( i \).

One can see that diffusion velocities and total heat flux depend not only on the gradients of gas temperature but also on the gradients of all level populations and number density of atoms with corresponding diffusion coefficients. The method of the calculation of the transport coefficients in the state-to-state approach is given in [3] and [9] where after some simplifications they are expressed in terms of \( n_i, n_O, T \) and elastic collision integrals. For the calculation of all diffusion and heat conductivity coefficients the state-to-state vibrational distributions found in the boundary layer in Ref. [10] have been used.

The boundary layer equations for a stationary flow in the vicinity of the stagnation point rewritten using the Lees-Dorodnitsyn coordinate transformation take the following form:

\[
\dot{c}_i'' + f'' S_{c} c_i' = S_i, \quad i = 0, 1, \ldots, 33
\]

(4)

\[
\dot{\theta}'' + f'' P_r' \dot{\theta}' = S_T
\]

(5)

where equations (4) for \( i = 0, 1, \ldots, 32 \) are the equations for the mass fractions \( c_i \) of molecules at the bounded vibrational levels, \( i = 33 \) corresponds to atomic mass fraction \( c_O \), and equation (5) is the energy conservation equation. Here \( f'' \) is the stream function, \( \theta \) is the reduced temperature \( P_r' \), \( S_{c} \) are the Prandtl and Schmidt numbers (they are supposed to be constant, \( S_{c} = 0.49, P_r = 0.71 \)). The derivatives have been done with respect to the surface normal co-ordinate \( \eta \). The source terms \( S_i \) and \( S_T \) describe, respectively, vibrational energy exchanges and dissociation-recombination in the gas phase and at the surface [10]:

\[
O_2(i) + O_2(k) \rightleftharpoons O_2(i-1) + O_2(k + 1)
\]

(6)

\[
O_2(i) + O_2 \rightleftharpoons O_2(i-1) + O_2
\]

(7)

\[
O_2(i) + O \rightleftharpoons O_2(i-1) + O
\]

(8)

\[
O_2(i) + \text{wall} \rightarrow O_2(i-1) + \text{wall}
\]

(9)

It is supposed that dissociation and recombination proceed only through the pseudo-level located just above the last bounded vibrational level [4]. From this point of view, dissociation and recombination in the gas phase are treated as VV and VT energy exchange processes involving the pseudo-level. Recombination and dissociation at the catalytic surface is described by two main mechanisms: the Eley-Rideal mechanism [7, 10]

\[
O + O' \rightleftharpoons O_2(i) + \text{wall}
\]

(10)

and the Langmuir-Hinshelwood one [7, 10]

\[
O' + O' \rightleftharpoons O_2(i) + \text{wall}
\]

(11)

\( O' \) is an adatom of the surface. Another possible mechanism

\[
O_2(i) + \text{wall} \rightarrow O + O
\]

(12)

has also been taken into account.
**BOUNDARY CONDITIONS**

Now we consider the boundary conditions for Eqs. (4) and (5). At the external edge of the boundary layer the gas temperature is fixed as a parameter $T_e$, and the level populations are supposed to follow the thermal equilibrium Boltzmann distribution with the gas temperature $T_e$. On the surface the gas temperature is also fixed $T = T_w$. Three different models are investigated for the mass fractions of vibrational species and atoms.

The first model assumes that the surface is totally non-catalytic. This model is referred hereafter as "nCnDnD" (no catalyticity, no dissociation, no deactivation). In this case:

$$\frac{\partial c_i}{\partial \eta} |_{w} = 0, \quad i = 0, \ldots, 33 \quad (13)$$

Then, a partially catalytic silica surface has been considered, the processes of heterogeneous recombination and dissociation (Eqs. (10)–(12)) as well as oxygen molecules deactivation (Eq. (9)) have been taken into account. This model is subsequently called "CDD" (catalyticity + dissociation + deactivation). In this case, the conditions for $c_j$ and $c_O$ at the wall read [10]:

$$\frac{\partial c_i}{\partial \eta} |_{w} = -\frac{\gamma_j}{D} \sqrt{\frac{kT}{2\pi m}} c_o + \gamma_{\text{diss}} c_i - \gamma_{\text{deact}} c_i + \gamma_{\text{deact}} c_{i+1}, \quad i = 0 \div 32 \quad (14)$$

$$\frac{\partial c_O}{\partial \eta} |_{w} = \sum_i \frac{\gamma_i}{D} \sqrt{\frac{kT}{2\pi m}} c_o - \sum_i \gamma_{\text{diss}} c_i \quad (15)$$

where recombination coefficient $\gamma_j$ represents the ratio of the flux of atoms recombining on the surface to the flux of atoms impinging the surface; the diffusion coefficient $D$ is assumed to be independent of the vibrational level number, the values of the diffusion coefficients are taken from Refs. [11] and [12]. We would like to note that in the right hand sides of Eqs. (14) and (15), the first term is due to recombination at the surface, the second one is due to heterogeneous dissociation, and the third and fourth ones in Eq. (14) are caused by deactivation at the wall.

The third model takes into account only heterogeneous recombination (direct reactions Eqs. (10)–(12)), this model is named as "CnDnD" (catalyticity, no dissociation, no deactivation). For a silica surface, the probability of oxygen recombination to each vibrational level has been calculated by Cacciatore et al [6, 7, 10] by means of quantum-classical molecular dynamics approach. The dissociation probability $\gamma_{\text{diss}}$ as well as the deactivation one $\gamma_{\text{deact}}$ have been estimated in Ref. [10].

The rate coefficients of the gas phase reactions (Eqs. (6)–(8)) are the same as the ones used in Ref. [13] where the results of accurate quantum-classical calculations of rate coefficients performed in Refs. [14] and [15] have been interpolated in a wide temperature range.

**RESULTS**

Eqs. (4) and (5) with boundary conditions in Eqs. (13), (14) and (15) have been solved numerically using a finite difference method described in details in Refs. [4] and [10]. The variables $c_i$, $c_O$, $T$ as well as their gradients have been found along the coordinate $\eta$. Then, this solution has been inserted into the kinetic transport theory algorithm [3, 9] to compute the diffusion and heat conductivity coefficients and the total heat flux. The heat flux sensitivity to the catalytic properties of the surface has been studied, and some interesting effects have been observed.

In the present section, we discuss the non-equilibrium vibrational distributions, gas temperature, and then heat fluxes and dissociation rate coefficients calculated using the three surface catalyticity models discussed previously: CDD, CnDnD and nCnDnD. The conditions at the high temperature edge of the boundary layer are: $T_e = 7000$ K, $p_e = 1000$ Pa, while the wall temperature is $T_w = 1000$ K.

First, let us consider the reduced O$_2$ level populations $n_i/n$. Figure 1 presents $n_i/n$ versus vibrational quantum number $i$ for different values of coordinate $\eta$ ($\eta = 0$ at the surface, $\eta$ increases to the external edge of a boundary layer). Three cases are compared: CDD model (catalytic wall with dissociation and deactivation); CnDnD model (catalytic wall neglecting dissociation and deactivation); nCnDnD model (completely non-catalytic wall). One can see the evolution of vibrational distributions across the boundary layer starting from the extremely non-equilibrium distribution in the vicinity of the wall towards the thermal equilibrium imposed at the external edge. The results for
the non-catalytic wall look similar to those reported for a 5 species mixture[13] (N₂, N, O₂, O, NO). The vibrational distributions present long declining plateaux due to the recombination process in the gas phase. Near the surface the plateau is quite stable. Note however that the concentration of molecules is very small in all the points of the boundary layer. Distributions change dramatically when recombination at the surface is taken into account. This reaction leads to a significant increase of O₂ concentration close to the surface and thus to much higher populations than in the previous case. The vibrational distribution at the surface is not completely smooth due to the form of the used state-to-state rate coefficients of the recombination catalytic process [10]. In the case of the complete CDD model, heterogeneous dissociation diminishes noticeably the concentration of molecules and therefore level populations near the wall compared to the CnDnD model. The distinction between CDD and CnDnD vibrational distributions at the surface is mainly due to dissociation, the influence of deactivation on the distribution is shown to be weak [10]. For the CDD model the non-smooth distribution at η = 0 is very pronounced, this behaviour is due to the non-monotonous character of recombination probabilities [10] and, perhaps, some overestimation of the dissociation rate coefficient.

Figures 2a,b depict the total heat flux (Fig. 2a) and Fourier flux due to thermal conductivity \( q_F = -\lambda \nabla T \) (Fig. 2b) calculated using the current three surface interaction models. It is seen that near the surface the CDD model gives a qualitatively different behaviour of the heat flux compared to the other two models. For the CDD model, the absolute value of \( q \) at the surface is much greater, then it decreases rapidly with η, and for η > 1 the solutions obtained with the CDD and nCnDnD models become close to each other. Comparison of the total fluxes obtained with the CDD scheme and neglecting dissociation and deactivation (CnDnD) shows an essential discrepancy practically in the whole

FIGURE 1. Reduced level populations, \( n_i/n \), as functions of i at different η.
range of $\eta$. These peculiarities can be explained after examination of the contribution of various processes to the heat flux. First, let us consider the Fourier flux (Fig. 2b). One can notice that a noticeable difference between the Fourier fluxes obtained using the CDD and CnDnD models manifests itself only close to the surface, at $\eta > 1.5$ the two fluxes are nearly the same. Such a behaviour near the wall is governed by the temperature gradients: the CDD models gives the highest temperature gradient at $\eta < 1$. A significant distinction between the total fluxes given by the CDD and CnDnD models shows the important role of heterogeneous dissociation and deactivation in the case of a partially catalytic surface. Recombination at the surface augments considerably the concentration of molecules, and this effect must be compensated by the corresponding reverse process. Taking into account only recombination at the wall and neglecting dissociation at the same time leads to an inadequate description of the heat flux. Thus, a strong discrepancy between the total heat fluxes for CDD and CnDnD models (see Fig. 2a) is dictated mainly by the different character of the $O_2$ and $O$ concentration gradients (in the CnDnD case the gradients are too high). Concerning the case of a completely non-catalytic surface (nCnDnD), the heat flux is determined only by thermal conductivity, the values of $q$ and $q_F$ coincide within 1%. It means that if one neglects recombination, dissociation and deactivation at the wall, then in some cases it is sufficient to use the Fourier law for the heat flux evaluation. Nevertheless, one should be careful using such an approximation: in Ref. [1] it is shown that for a $N_2/N$ mixture the contribution of diffusion processes can reach 60-65% even if the surface is absolutely non-catalytic. Finally, one can conclude that although the nCnDnD model gives a good agreement with the CDD scheme at $\eta > 1$, it is better to use the CDD model and the expression in Eq. (3) instead of the Fourier law (especially near the wall) in order to get satisfactory accuracy.

The next figures (Figs. 3a,b) represent the contribution of various transport processes to the total energy transfer. Among the diffusion processes one can distinguish thermal diffusion, mass diffusion of chemical species and diffusion of vibrational energy by excited molecules. In Figs. 3a,b the CDD (a) and CnDnD (b) models are considered. The corresponding plot for the nCnDnD model is not reported, because from the previous discussion it is clear that in this case the contribution of diffusion to the heat flux is negligible. Figure 3 shows that for both the CDD and CnDnD models the heat flux is scarcely affected by thermal diffusion (its maximum contribution does not exceed 6% in the vicinity of the surface and then decreases to 3%). For the CDD model, (Fig. 3a) the influence of mass diffusion of atoms is also small, and the main role in the heat transfer belongs to heat conductivity and diffusion of vibrational energy. Near the wall a competition of these two processes is observed. In the case of CnDnD model, the contribution of heat conductivity, mass diffusion and diffusion of vibrational energy is of the same order of magnitude. A similar tendency has been found in Ref. [2] where the partially catalytic surface without dissociation has been considered for different conditions.

The subsequent discussion is devoted to the rate coefficients of dissociation in the gas phase. In many essentially non-equilibrium flows a non-Arrhenius temperature dependence of averaged dissociation rate coefficients has been discovered [13, 16, 17]. The present investigation confirms this statement. The global rate coefficients can be expressed in terms of the state-to-state coefficients [17]:

$$k^{(M)}_{diss} = \frac{1}{n_{O_2}} \sum_i n_i k^{(M)}_{i,diss}$$  \hspace{1cm} (16)
FIGURE 3. Contribution of various processes to the heat flux. CDD (a) and CnDnD (b) models. Curves 1: total heat flux; 2: Fourier flux; 3: flux due to thermal diffusion; 4: flux due to mass diffusion of atoms; 5: flux due to diffusion of vibrational energy.

FIGURE 4. Averaged dissociation rate coefficients $k^{(M)}_{\text{diss}}$ (cm$^3$/s) and corresponding Arrhenius coefficients for CDD model (a), and ratio $k^{(at)}_{\text{diss}}/k^{(at)}_{\text{eq}}$ for three models (b) as functions of $\eta$.

For the ladder climbing model, as dissociation proceeds only through the last bounded level $L$, this definition is reduced to the following one:

$$k^{(M)}_{\text{diss}} = \frac{n_L}{n_{O_2}} k^{(M)}_{L,\text{diss}}$$

(17)

Coefficient $k^{(M)}_{L,\text{diss}}$ is determined by the rate coefficients of VV and VT vibrational energy exchanges.

Figure 4a plots the averaged rate coefficients $k^{(\text{mol})}_{\text{diss}}$ and $k^{(at)}_{\text{diss}}$ for dissociation through the collisions with molecules and atoms respectively, across the boundary layer (CDD model). The corresponding thermal equilibrium Arrhenius rate coefficients $k^{(\text{mol})}_{\text{eq}}$ and $k^{(at)}_{\text{eq}}$ are also presented. One can see a quite different behaviour of the rate coefficients calculated using the state-to-state distributions compared to the Arrhenius ones, close to the surface the curves have an opposite tendency. Figure 4b displays the ratio $k^{(at)}_{\text{diss}}/k^{(at)}_{\text{eq}}$ computed for the three models discussed previously. It can be noticed that taking into account heterogeneous recombination, dissociation and deactivation produces a decrease of the ratio $k^{(at)}_{\text{diss}}/k^{(at)}_{\text{eq}}$ in the gas phase.
It should be noted that the limit value $\eta = 8$ is sufficient for the calculation of the main macroscopic parameters: gas temperature, density, species concentrations, heat flux. The exception is for the dissociation rate coefficients. These quantities do not converge to the equilibrium values at $\eta = 8$, and for the correct prediction of $k_{\text{diss}}^{(M)}$ a greater limit value $\eta = 16$ has been chosen. It is connected with peculiarities of the ladder-climbing model: in this case, the dissociation rate coefficients are determined mainly by the population of the last vibrational states, and those states are strongly disturbed by dissociation. In the present calculation, the populations of the highest 2–3 vibrational levels do not reach their equilibrium values at $\eta = 8$, and therefore coefficients $k_{\text{diss}}^{(M)}$ behave similarly. One can expect that using another dissociation model, for instance the Treanor-Marrone one, will provide a better convergence and a good accuracy of the solution at $\eta = 8$.

**CONCLUSIONS**

Non-equilibrium vibrational-chemical kinetics and transport properties in the O$_2$/O mixture flow in the boundary layer adjacent to a catalytic silica surface have been investigated by using the detailed state-to-state approach. Three different models of the catalytic activity have been examined: (1) a partially catalytic surface model which accounts for heterogeneous recombination, dissociation and deactivation of excited vibrational states; (2) a model that takes into account only heterogeneous recombination and neglects reverse dissociation process and deactivation at the wall; and finally, (3) a totally non-catalytic model.

The state-to-state vibrational distributions as well as the gas temperature and chemical species concentrations have been computed across boundary layers in the vicinity of a stagnation point. The influence of surface catalyticity models on the vibrational distributions and other macroscopic parameters has been estimated. In all cases essentially non-equilibrium distributions have been found for the conditions investigated. For the case of a non-catalytic surface, the concentration of molecules near the wall as well as its change across the boundary layer are shown to be low. For the catalytic surface, neglecting dissociation at the wall leads to excessively high variation of species concentrations and their gradients across the flow. Taking into account all heterogeneous processes provides a fast rise of the gas temperature just near the wall compared to the other two models.

Then the calculated macroscopic parameters and vibrational distributions have been used as input data for evaluation of the total heat flux, which in the state-to-state approach depends on the gradients of all level populations, atomic number density and gas temperature. The role of surface catalysis and the contribution of various processes to the heat transfer have been estimated. In particular, it is shown that using the non-catalytic boundary conditions gives an underestimation of the heat flux near the surface, in this case the heat transfer is determined mainly by thermal conduction; neglecting dissociation at the surface leads to a big discrepancy between the calculated heat fluxes practically in the whole region considered. The contribution of vibrational energy diffusion to the heat transfer is particularly important when the complete kinetic scheme at the surface is applied. The role of thermal diffusion in the heat flux is quite weak in all cases examined. In conclusion, it can be pointed out that the self-consistent CDD model taking into account heterogeneous recombination, dissociation and deactivation should be used in order to get adequate values of the total heat flux.

Finally, the non-equilibrium rate coefficient of dissociation in the gas phase across the boundary layer has been calculated, and its temperature dependence is found to be essentially non-Arrhenius for all models of surface catalyticity.

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