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Electron and Vibrational Kinetics in the Boundary Layer of Hypersonic Flow

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A simplified fluid dynamic model of the boundary layer in hypersonic flow has been coupled with complete vibrational kinetics for pure nitrogen. We focus our attention on the electron–molecule collisions and calculate the rate coefficients of such processes by solving the stationary Boltzmann equation for electron kinetics. The role of ionization degree in affecting vibrational and electron energy distributions has also been investigated.

Nomenclature

c_N = mass fraction of nitrogen atoms
c_v = mass fraction of nitrogen vth vibrational level
$\dot{c}_x$ = mass fraction collision frequency
E = electric field
$\bar{E}_{elect}$ = electron mean energy
E_v = energy of vth vibrational level
E_x = threshold energy
$e-e$ = electron–electron coulomb collisions
el = elastic collisions
e = electrons
$e-M$ = electron–molecule collisions
$f(\eta)$ = stream function
J_x = flux terms in electron energy space
K_x = rate coefficients
k = Boltzmann constant
Le = Lewis number
N = nitrogen atoms
N_e = electron density
N_2 = nitrogen molecules
$n(\varepsilon)$ = electron energy distribution function
P = gas pressure
Pr = Prandtl number
$Q_p(\varepsilon)$ = electron collision rate coefficients for monoenergetic electrons
R_p = electron collision rate coefficients
Sc = Schmidt number
$S_{in,sup}$ = source terms in electron energy space
$S_{v,T}$ = source terms
T_e = temperature at the edge of the boundary layer
T_{elect} = electron temperature
T_g = gas temperature
T_w = surface temperature
t = time
v, b, w, d = vibrational quantum numbers
$v(\varepsilon)$ = electron speed
α = ionization degree
β = flow characteristic frequency
ε = electron energy
ε^* = electron collision threshold energy
η = coordinate perpendicular to the surface
η_{max} = boundary-layer thickness
ρ = mass density
ρ_v = mass density of the vth vibrational level
σ_p = electron–molecule/atoms collision cross sections

Subscripts
elect = electron
in = inelastic collisions
sup = superelastic collisions

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Introduction

In recent papers[1–5] hypersonic flow of molecular gases in the boundary layer surrounding a body has been studied using simplified fluid dynamic models in which a complete chemical kinetics has been taken into account.

In particular dissociation, recombination and vibrational kinetics in nitrogen flows have been studied by our group,[2–5] analyzing the role of each process in affecting vibrational distributions, temperature profiles, and temperature gradients (heat flux). Also, the role of multiquanta $V-T$ (Refs. 2–5) collisions between atoms and vibrationally excited molecules has been studied. In these papers we have completely neglected the presence of free electrons.

On the other hand, electron kinetics in nitrogen postdischarges have been studied by our group,[6] emphasizing the strong coupling of vibrationally excited states and free electrons. These conditions are very similar to those occurring in the boundary layer of a body hit by a hypersonic flow, the role of electrons being to exchange energy between the different vibrational levels.

Usually this problem has been solved by the fluid dynamic community by using a Maxwell distribution function for electrons. This assumption is dropped in this article where we present preliminary results obtained by coupling the vibrational kinetics and the Boltzmann equation for free electrons. In doing so we assume a flat profile of ionization degree in the boundary layer (i.e., we completely disregard ionization–recombination kinetics for free electrons). This assumption, even though not completely valid for hypersonic flow conditions, allows easy treatment of electron–molecule processes.

Numerical Model

The numerical model of boundary-layer hypersonic flow has been widely described in previous works.[1–5] It consists of performing self-similarity coordinate transformation to Navier–Stokes equations to obtain one-dimensional vibrational kinetics,[1–5]

$$\frac{\partial^2 c_v}{\partial \eta^2} + Scf(\eta)\frac{\partial c_v}{\partial \eta} = -S_v \qquad (1)$$

and T_g equation,[1-5]

$$\frac{\partial^2 T_g}{\partial \eta^2} + Prf(\eta)\frac{\partial T_g}{\partial \eta} = -LeS_T \tag{2}$$

from which we calculate the temperature profile and the vibrational distribution function (VDF) along a coordinate η normal to the vehicle surface. The c_v are the local mass fraction ρ_v/ρ of the vth species (for $v = 0 \div 45$ it is nitrogen molecules in vth vibrational state, and for $v = 46$ it refers to nitrogen atoms).

The $f(\eta)$ is calculated according to the Blasius approximation, the validity of which requires constant Prandtl and $\mu\rho$ values in the boundary layer (μ is the viscosity). These requirements are not completely satisfied in our conditions. Note, however, that for the ionization degrees considered in the present article, free electrons do not appreciably change both the viscosity and the translational thermal conductivity of the mixture. Both S_v and S_T are source terms because of collision processes. Note that we are neglecting radiation transfer that could be important in the calculation of surface heat transfer in thin boundary layers.

The source terms can be expressed as the sum over all the processes considered (see Refs. 1–5 for details),

$$S_v = a\sum_{d,w,b} \dot{c}_{(v,b)\leftrightarrow(w,\,d)}$$
$$S_T = a\sum_{d,w,b} \frac{E_{(v,b)\to(w,d)}}{c_p}\,\dot{c}_{(v,b)\leftrightarrow(w,d)} \tag{3}$$

where v, b are the indexes of the reacting species; w, d are the indexes of the products; the energy exchanged in the direct process is $E_{(v,b)\to(w,d)}$; c_p is the constant pressure specific heat including only translational and rotational contributions; and

$$\dot{c}_{(v,b)\leftrightarrow(w,d)} = K_{(w,d)\to(v,b)}c_w c_d - K_{(v,b)\to(w,d)}c_v c_b$$
$$a = \frac{ScP}{kT_g\beta(1 + c_N)} \qquad \beta = \|\text{grad } P\|_{\text{stag}} \tag{4}$$

The pressure gradient at the stagnation point β can be considered as representative of the inverse of the residence time of a particle in a point of the boundary layer.

The vibrational kinetics include v–v (vibration–vibration), v–T (vibration–translation) dissociation and recombination processes.[1-5] Recombination selectively pumps levels $v = 25$ and $v = 45$ as discussed in Refs. 1–5.

Electron kinetics have been studied solving the Boltzmann equation for electron kinetics in homogeneous, quasi-isotropic approximation,[7]

$$\frac{\partial n(\varepsilon)}{\partial t} = -\frac{\partial(J_E + J_{\text{el}} + J_{e-e})}{\partial \varepsilon} + S_{\text{in}} + S_{\text{sup}} \tag{5}$$

where J_E, J_{el}, and J_{e-e} are the contributions because of E, el, and (e–e). These terms represent diffusion of electrons in energy space, S_{in} and S_{sup} are source terms from inelastic and superelastic collisions.[7-9] In the first case, electrons lose energy, the reverse being true for superelastic collisions. The two terms have the form

$$S_x = \sum_p N_s[Q_p(\varepsilon + \varepsilon^*)n(\varepsilon + \varepsilon^*) - Q_p(\varepsilon)n(\varepsilon)] \tag{6}$$

where the x can be inelastic or superelastic, p numbers the collision process, N_s is the particle density of the molecules involved in the collision, ε^* is the energy exchanged in the collision (positive for inelastic and negative for superelastic), and $Q_p(\varepsilon)$ is the collision rate for electrons with energy ε, given by

$$Q_p(\varepsilon) = \nu(\varepsilon)\sigma_p(\varepsilon) \tag{7}$$

where ν is the electron speed and σ_p is the cross section of the process.

Physically, Eq. (5) is valid when electron elastic collision frequency is higher than inelastic and superelastic ones.[7]

Moreover, since electron diffusion is much faster than vibrational kinetics (because of the corresponding rate coefficients), we can assume that electron kinetics will follow in a stationary way the vibrational kinetics. Therefore, electron energy distribution functions (EEDFs) can be calculated at the stationary conditions with the algorithm discussed by Capriati et al.[8]

The linking of the two models considers as input of the electron kinetics, the molecular density, the molar fraction of atomic and molecular nitrogen, vibrational excited states fraction [$N_2(v/N_2]$ [i.e., N_s in Eq. (6)], and the local gas temperature, calculated by solving the system of Eqs. (1) and (2), and, as input of vibrational kinetics equations, the rate coefficients of the vibrational excitation (inelastic) and deactivation (superelastic) from electron impact processes:

$$e + N_2(0) \Leftrightarrow e + N_2(1 \div 8) \tag{8}$$

The model of N_2 considered for the electron kinetics is described by Capitelli[6] and Colonna et al.[9]; and the electron impact cross sections for molecular and atomic nitrogen have been taken from Phelps et al.[10] and Cacciatore et al.,[11] respectively.

Another approximation made in this article is to consider frozen ionization kinetics. Therefore, we consider α (which is the ratio between electrons and heavy particle densities), as a parameter independent of the position. This parameter is very important for the model because the electron collision frequency is proportional to α.

The bulk of our results has been obtained in the absence of an electric field. These conditions are similar to those occurring in postdischarge conditions[6,9] (soon after the switchoff of the electric field), where a strong coupling between nonequilibrium vibrational distributions and non-Maxwell electron energy distribution functions have been observed. The presence of an electric field has also been studied by considering it as a free parameter.

In the electron kinetics e–e and e–i coulomb collisions have been neglected because their insertion needs large computational times because of the nonlinear terms introduced in the Boltzmann equation by e–e collisions (see Ref. 9).

Note, however, that in some of the reported conditions ($\alpha \geq 10^{-4}$) e–e and e–i collisions can be important.[9]

The vibrational kinetics and the temperature equation need boundary conditions on the vehicle surface ($\eta = 0$) and at the edge of the boundary layer ($\eta = \eta_{\max}$). We fixed the temperatures on both extremes of the boundary layer (T_w on the wall and T_e at the edge). For the vibrational kinetics we assume that at the edge of the boundary layer the VDFs are characterized by a Boltzmann distribution at $T_g = T_e$ and that the surface is not catalytic (VDF derivatives are null at $\eta = 0$). The atomic mass fraction has the same boundary conditions as the vibrational distribution.

The results shown in this work have been calculated fixing the surface temperature at $T_w = 1000$ K, while two edge tem-

Table 1 Considered cases

Case	T_e, K	Atoms
(a)	7000	No
(b)	7000	Yes
(c)	5000	No
(d)	5000	Yes

peratures (T_e = 5000 K and T_e = 7000 K) have been considered. The latter determines the atomic mass fraction in all of the boundary layers and, as a consequence, the collision frequency of processes that involve atoms.[1-5]

To analyze the role of collisions with atoms, we perform calculations both including and neglecting the presence of atoms. In brief, we explore conditions listed in Table 1. Note that cases (a) and (c) do not consider the processes of dissociation and recombination in the master equations, while cases (b) and (d) do. In all the cases considered, the pressure has been fixed at 10^5 Pa and the parameter β at 10^5 s^{-1}. Note, however, that the results mainly depend on the ratio P/β.

Output Description

The model described previously gives as output the VDF, the atomic mass fraction (AMF), the EEDF, and the gas temperature profile.

Note that vibrational and electron energy distributions are not calculated by commonly used fluid dynamical numerical codes, which on the contrary characterize them with different temperatures. This procedure implicitly assumes the existence of a Boltzmann distribution for the vibrational states and a Maxwell distribution function for the translational energy of free electrons.

In our case, since the distributions we are dealing with can be very far from Maxwell or Boltzmann, the concept of temperature loses a physical meaning. However, it is still possible to define a temperature for each distribution, referring to quantities that are directly related to the temperature in the case of Boltzmann or Maxwell distributions.

We define an electron temperature as

$$T_{\text{elect}} = \tfrac{2}{3}\bar{E}_{\text{elect}} \tag{9}$$

where

$$\bar{E}_{\text{elect}} = \int_0^\infty \varepsilon \cdot \text{EEDF}(\varepsilon) \cdot d\varepsilon \tag{10}$$

is the electron mean energy.

The vibrational temperature is defined in a different way: results calculated neglecting $e-M$ collisions[1-5] show that at low vibrational quantum number ($v \leq 10$) the VDFs present a Boltzmann trend, therefore, we chose as T_v the quantity

$$T_v = [(E_1 - E_0)/k]\ell n(c_0/c_1) \tag{11}$$

where E_1 and c_1 are, respectively, the energy of the first vibrational excited level and the molar fraction of molecules in that level; while E_0 and c_0 refer to the ground state. From the EEDFs it is possible to calculate $e-M$ rate coefficients. From the vibrational kinetics point of view the rate coefficients of electron collision processes are proportional to α, therefore,

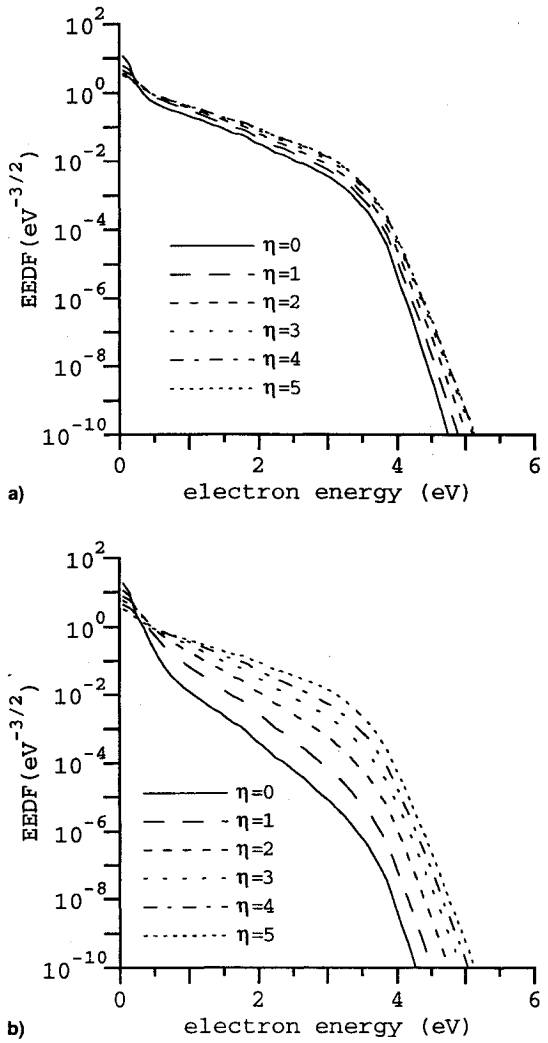

Fig. 1 EEDFs at different distances η from the surface without $A-M$ collisions at α = a) 10^{-7} and b) 10^{-3} [conditions: case (a) of Table 1].

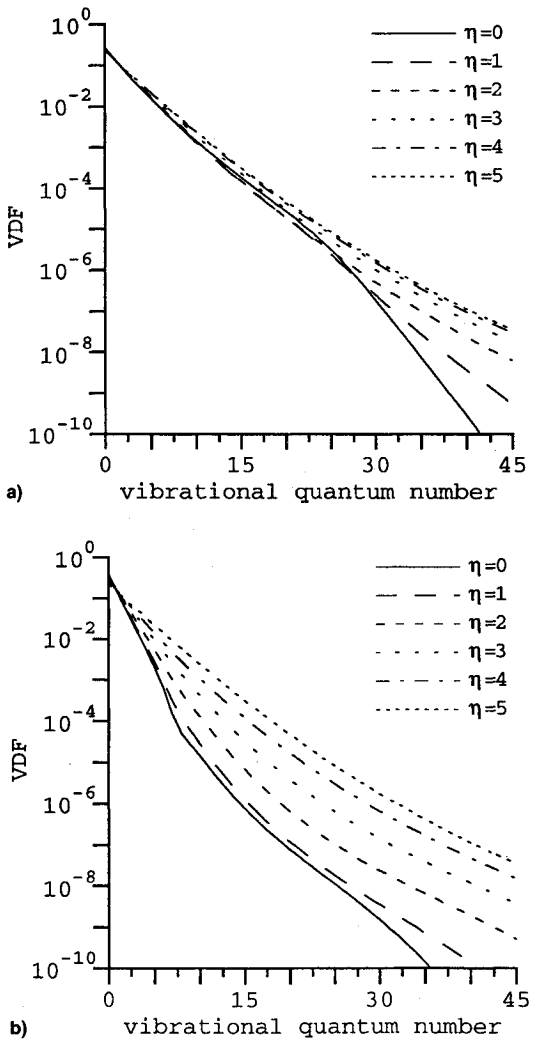

Fig. 2 VDFs at different distances η from the surface without $A-M$ collisions at α = a) 10^{-7} and b) 10^{-3} [conditions: case (a) of Table 1].

we consider as a rate coefficient of the process p, the quantity,[7-9]

$$R_p = \int_0^\infty Q_p(\varepsilon) \cdot \mathrm{EEDF}(\varepsilon) \cdot \mathrm{d}\varepsilon \tag{12}$$

where the symbols are the same as Eq. (7). This quantity contributes to the source terms of Eq. (1), adding other terms at Eq. (3) of the same form as those in Eq. (4), where the rates K assume the value

$$K_p = (1 + c_N)\alpha R_p \tag{13}$$

Equation (13) suggests comparing αR_p (for $e-M$) with the atom–molecule ($A-M$) collision rates to understand which is the dominant process. In this work we focus our attention on $e-M$ vibrational excitation ($p = 0 \rightarrow v$) and deactivation ($p = v \rightarrow 0$).

Results: EEDFs and VDFs

To understand the role of $e-M$ collisions it is important to analyze EEDFs (Fig. 1) and VDFs (Fig. 2) in different conditions. In particular we compare the distributions in the case where the $a-M$ collisions have no effect (Fig. 1), with that one in which these collisions are important (Fig. 2) for the vibrational kinetics. The results reported in Figs. 1 and 2 refer to case (a) of Table 1. Similar results have been obtained in the other cases.

In Fig. 1a it can be seen that, at low ionization degree, the EEDFs change slowly with the distance η from the vehicle surface. The same characteristics can be observed for VDFs (Fig. 2a), especially at low vibrational quantum number ($v < 20$). At high α, both EEDFs (Fig. 1b) and VDFs strongly depend on the distance from the vehicle, and in particular they become lower moving towards the surface. From these results it can be deduced that electron kinetics are governed by the VDF. Note, in fact, that for the studied case [i.e., case (a)], where recombination and dissociation kinetics have been neglected), electron–atom collisions have the same effect in all of the boundary layers because the mass fraction of atomic nitrogen is constant. Moreover, the effects of coupling electron and vibrational kinetics in the boundary-layer equations can be deduced from Figs. 1 and 2. The EEDF gains energy only from vibrational excited states of molecular nitrogen by means of superelastic collisions [reverse processes in Eq. (8)]. These processes are very efficient because they involve low-energy electrons; in fact, the EEDFs have very high values at low electron energies. As a consequence, superelastic collisions cool the VDF (because of the energy transfer to electrons). The final result is that both EEDFs and VDFs become colder moving from the external to the surface. The effect of $e-M$ collisions depends on the distance from the external, where the distributions are fixed. The characteristic length of the $e-M$ process is a function of the product between the diffusion time and the $e-M$ collision frequency. Another important feature is that EEDFs and VDFs are far from Maxwell and Boltzmann distributions. This last point can be better appreciated remembering that equilibrium distributions (Boltzmann and Maxwell) should appear as straight lines in the plots of Figs. 1 and 2.

To study the role of the ionization degree on EEDFs and VDFs is useful to focus our attention on the distributions near

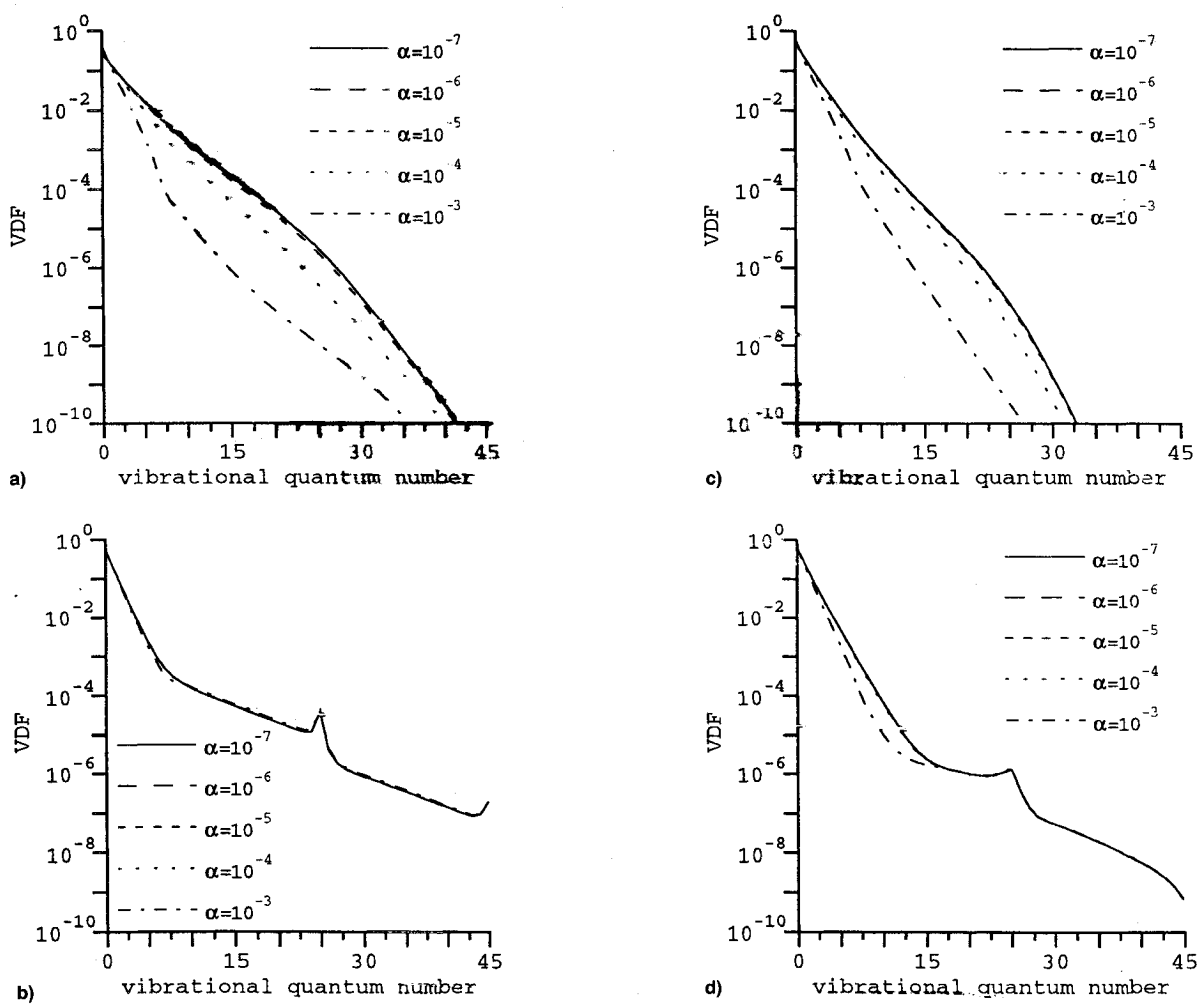

Fig. 3 VDFs adjacent to the surface at different values of α [labels a), b), c), and d) refer to the conditions listed in Table 1].

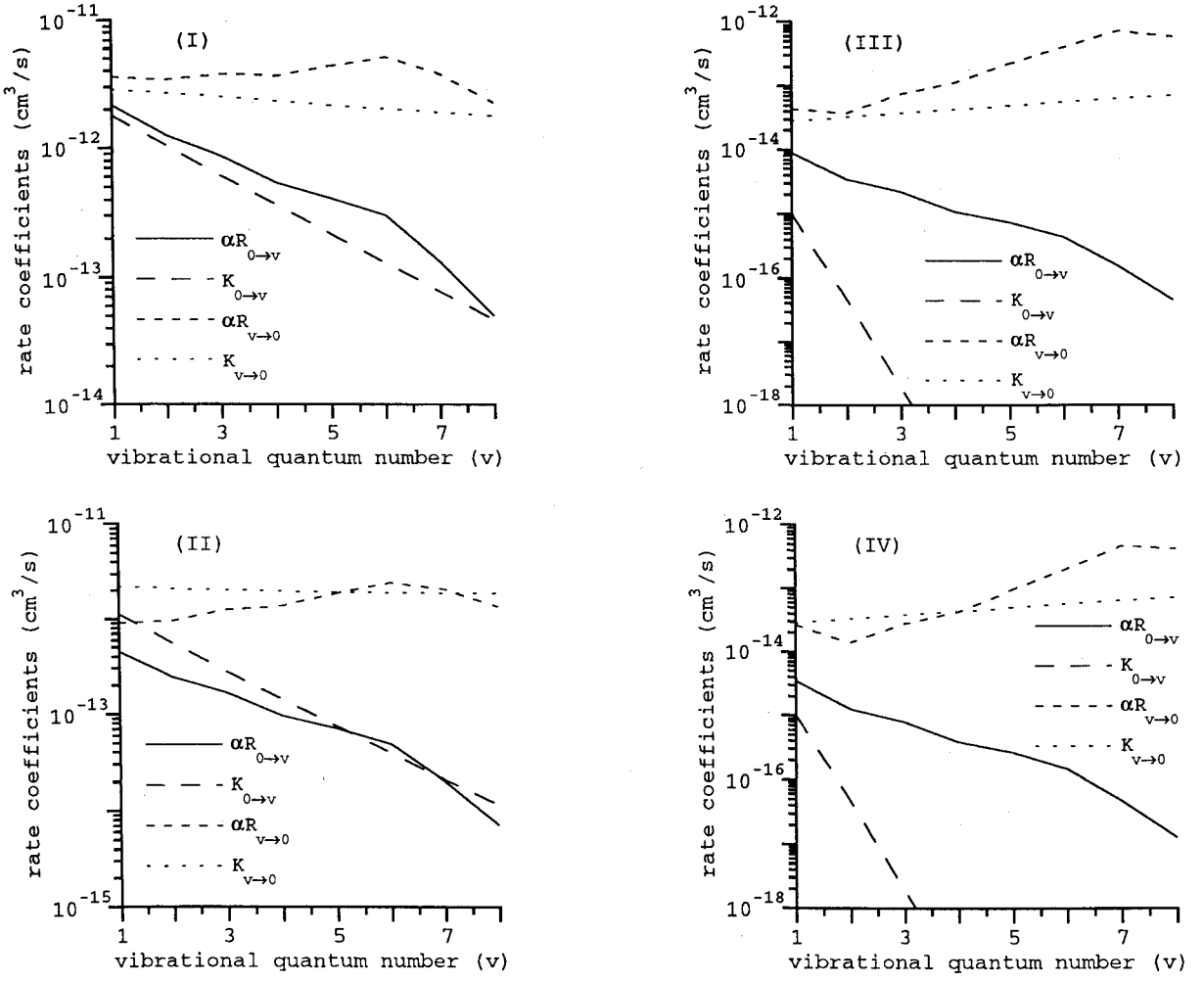

Fig. 4 $e-M$ (R) and $v-T$ (K) by atoms rate coefficients as a function of the vibrational quantum number at the external (I and II) and at the vehicle surface (III and IV) [I and III refer to case (b) and II and IV refer to case (d) of Table 1], at $\alpha = 10^{-3}$.

the surface, where the effect of $e-M$ collisions is more important. In Figs. 3a–3d we have reported the VDFs for the different conditions of Table 1 (the letter that labels the graph refers to the column case in the table). We observe that $e-M$ collisions are important only in the absence of the recombination–dissociation processes [i.e., for cases (a) and (c) of Table 1], losing their importance in the presence of the recombination–dissociation processes [i.e., for cases (b) and (d)]. Note that in this last case the maximum in the vibrational distribution at $v = 25$ (see Figs. 3b and 3d) is the result of the selective pumping of this vibrational level by the recombination process (see Refs. 1–5). Since the molar fraction of atomic nitrogen strongly increases with increasing T_e, the $v-T$ terms dominate the $e-M$ ones at $T_e = 7000$ K, while at $T_e = 5000$ K, $v-T$ and $e-M$ terms have similar importance.

When $A-M$ collisions are neglected (Figs. 3a and 3c), $e-M$ collisions are very important, cooling the VDFs as seen in Fig. 2. It seems that this phenomenon behaves like a phase transition in which α is the order parameter: when $\alpha < 10^{-5}$ $e-M$ collisions have no effect, the reverse being true for $\alpha > 10^{-5}$.

To understand this behavior it is useful to compare $v-T$ and $e-M$ rate coefficients in some fixed points of the boundary layer (i.e., at the external and near the vehicle surface). In Fig. 4 we have reported these rates for cases [(b) and (d)] in Table 1. It is evident that the governing processes are the deactivation of excited states (both for $e-M$ and $v-T$). Since the $e-M$ rates are proportional to the ionization degree [see Eqs. (12) and (13)], these rates will lose their importance at low ionization degrees.

Results: Temperatures

In the previous paragraph we have analyzed the behavior of electrons and vibrational state distributions. The quantities commonly considered in hypersonic fluid dynamics are the temperatures of each degree of freedom (i.e., gas, electron, and vibrational temperatures). The gas, vibrational, and electron temperatures are shown in Fig. 5 for conditions of case (b) of Table 1. The $e-M$ collisions have an appreciable effect on the temperature profiles for $\alpha \geq 10^{-4}$. In particular, their presence decreases all of the reported temperatures.

This behavior is a consequence of the VDFs cooling (see Figs. 2 and 3), because of the superelastic $e-M$ collisions. Therefore, an energy flux is established from translational to vibrational degrees of freedom, because of $v-T$ collisions (especially those with nitrogen atoms), to compensate the losses of vibrational energy because of superelastic collisions. In this way the gas temperature decreases.

The EEDFs follow the VDFs (as explained in the previous section), and therefore, T_{elect} also decreases.

The global effect is an energy flux from translation to vibration and then to electrons. In this way the heat flux to the vehicle surface decreases when the ionization degree increases, as can be seen in Fig. 6, where the temperature gradient percent variation (with respect to the case in which no electrons are present) as a function of α has been reported in the conditions listed in Table 1.

The greatest effect is observed in case (b) where the percent variation of the temperature gradient can be more than 15%. This feature can be explained by the fact that the prevalent

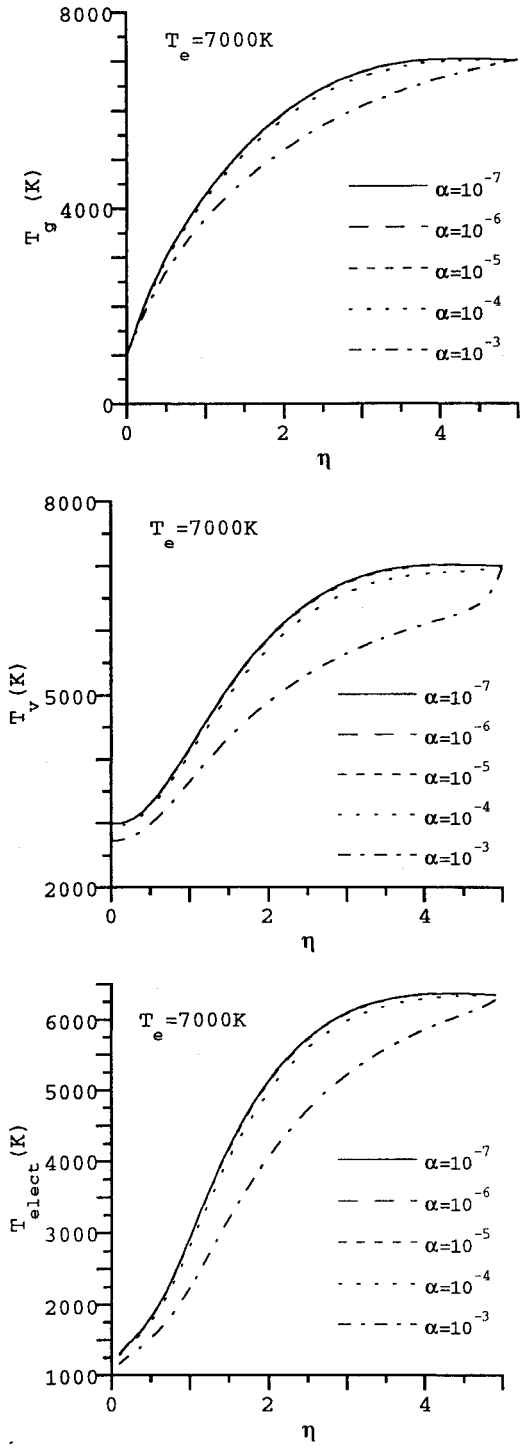

Fig. 5 Gas (g), vibrational (v), and electron (elect) temperatures at different α calculated for case (b) of Table 1.

processes are the $v-T$ by atom collisions, therefore, the higher the atom density, the higher the energy flux from translation to vibration.

A common assumption in the used hypersonic flow models is that electron temperature is linked to the vibrational one. The results we obtain are a little more complicated, showing a dependence of T_{elect} on both T_v and T_g.

Presence of Electric Fields

In previous papers we have completely neglected the possibility of the existence of electric fields as a result of the different mobilities of electrons and ions. In this case one should solve a Poisson equation to obtain the electric field to

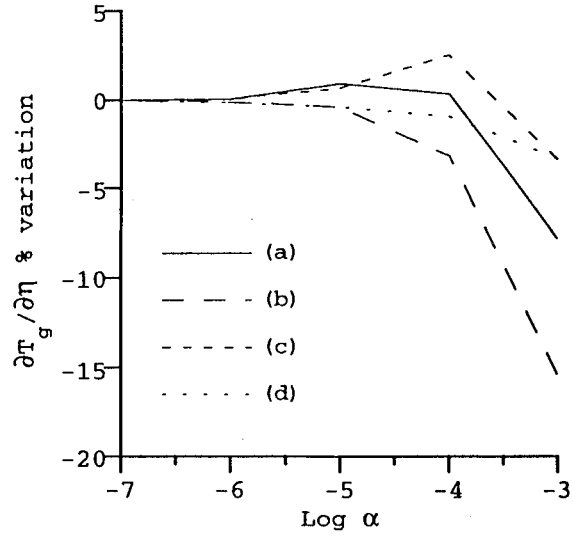

Fig. 6 Temperature gradient percent variation to the vehicle surface as a function of α for conditions listed in Table 1 (the curve labels refer to the column case in the table).

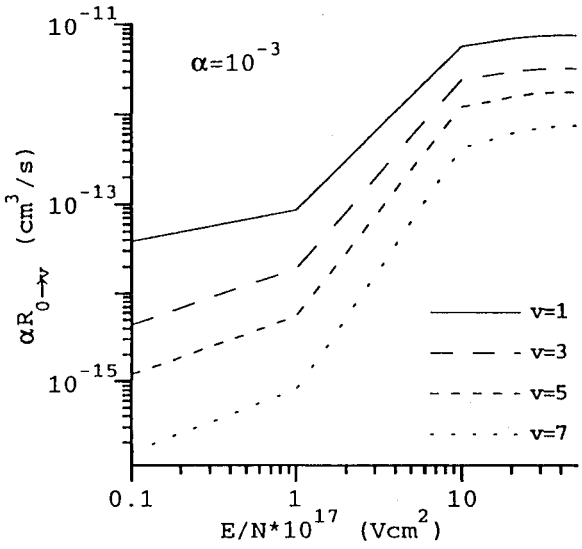

Fig. 7 Vibrational excitation $e-M$ rate (multiplied by $\alpha = 10^{-3}$) as a function of the reduced electric field (E/N).

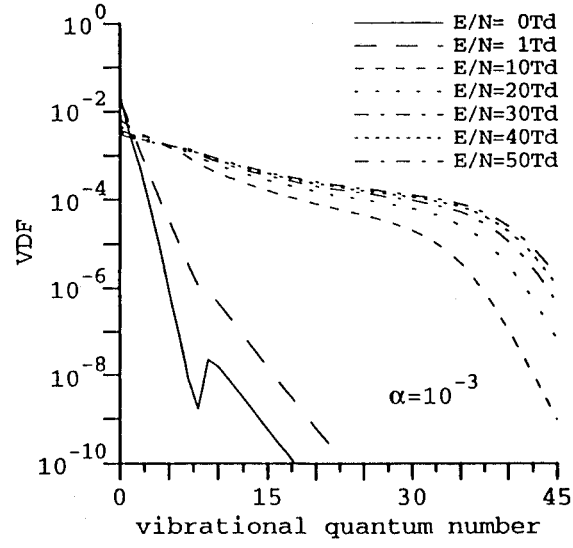

Fig. 8 VDFs adjacent to the vehicle surface ($\eta = 0$) as a function of the reduced electric field (E/N).

be inserted in the Boltzmann equation. This approach is beyond the scope of this article.

An estimation of the importance of electric fields in affecting the vibrational kinetics can be done by parametrizing E, i.e., by solving the Boltzmann equation with different E/N values (N is the total number of neutral particles).

A sample of results has been reported in Figs. 7 and 8 for conditions different from those reported in Table 1 (i.e., $P = 10^3$ Pa, $\beta = 10\ s^{-1}$, $T_e = 7000$ K, $T_w = 1000$ K, no atoms). All of the results refer to $\eta = 0$. In particular, Figs. 7 and 8 respectively report $e-M$ rates and VDFs as a function of the reduced electrical field E/N ($1T_d = 10^{-17}$ Vcm^2).

Reduced electrical fields higher than 10^{-16} Vcm^2 strongly affect the vibrational kinetics. In particular the inelastic $e-M$ collisions are able to introduce vibrational quanta in the vibrational manifold from the bottom. These quanta are then redistributed by $V-V$ energy exchange processes ending in a strong overpopulation of VDFs. The vibrational distributions near the surface (see Fig. 8) present a long plateau similar to the corresponding distributions occurring under plasma conditions (see e.g., Ref. 6).

Conclusions

In this article we have presented for the first time, to our knowledge, an attempt to couple electron and vibrational kinetics in the boundary layer surrounding a body hit by a hypersonic flow of active species including free electrons.

The results show a strong nonequilibrium character of both electron and vibrational distributions so that the fluid dynamic codes based on the concept of temperatures can be open to question.

The present results can be improved either by adding ionization–recombination kinetics for free electrons or by considering electron–electron and electron–ion collisions in the Boltzmann equation. The first improvement is of paramount importance since the assumption of constant ionization degree in the boundary layer is the weakest point of the present calculations.

Finally, we have shown the role of electric field, considered as a free parameter, in enhancing vibrational distributions as a result of the pumping of vibrational energy through electron–molecule collisions.

The present results, even though of a qualitative nature, indicate the importance of treating each vibrational level as a separate species and of solving an appropriate Boltzmann equation for non-Maxwellian electron energy distribution function.

Acknowledgments

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