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Non-Maxwell Behavior of Electron Energy Distribution Functions in Expanding Nitrogen Arcs

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The electron energy distribution function (eedf) in expanding nitrogen arcs has been obtained by solving a Boltzmann equation including elastic, inelastic, and superelastic terms. Different realistic hypotheses on the concentrations of vibrationally and electronically excited states as well as on the ionization degree have been assumed. The results show that eedf and related coefficients are strongly dependent on the concentrations of excited states that superimpose structures to the bulk of eedf.

Nomenclature

g_i = statistical weight of level i
In = flux term because of inelastic collisions
$In_{(\mathrm{electr})}$ = flux term because of inelastic electronic collisions
$In_{(\mathrm{ion})}$ = flux term because of ionization collisions
$In_{(\mathrm{rot})}$ = flux term because of inelastic rotational collisions
$In_{(\mathrm{vib})}$ = flux term because of inelastic vibrational collisions
n_{N_2} = nitrogen number density in the ground state
$n_{\mathrm{N}_2^*}$ = population density of the excited state
$n(u, t)$ = number density of electrons at energy u and time t
Sup = flux term because of superelastic collisions
$Sup_{(\mathrm{electr})}$ = flux term because of superelastic electronic collisions
$Sup_{(\mathrm{vib})}$ = flux term because of superelastic vibrational collisions
$v(u)$ = electron velocity at energy u
$(\partial J_{\mathrm{el}}/\partial u)_{e-e}$ = flux term because of electron–electron elastic collisions
$(\partial J_{\mathrm{el}}/\partial u)_{e-N}$ = flux term because of elastic collisions
σ_{in} = inelastic cross section
$\sigma^*(u)$ = superelastic cross section at energy u

I. Introduction

IN the last decade a large effort has been devoted to the coupling of an electron energy distribution function (eedf) to the distribution of vibrationally and electronically excited states under discharge and postdischarge conditions. The main result of these investigations concerned the role of superelastic (second-kind) collisions in altering the eedf. In particular, second-kind collisions involving vibrationally excited molecules are able to thermalize the eedf at the vibrational temperature of the molecules,[1] whereas second-kind collisions involving electronically excited states produce a highly structured eedf as a result of the heating of cold electrons by the excited state.[2] The effects become higher as the reduced electric field (E/N) sustaining the discharge grows smaller, thus becoming quite important in the postdischarge regime ($E/N = 0$). Many calculations were done by our group to show these effects for low-pressure discharge and postdischarge conditions when the translational temperature of the different components approximately equals the room temperature.[3]

There has been very little research concerning the extension of these ideas to expanding arc conditions because it is generally believed that the high ionization degrees present in these conditions are sufficient to Maxwellize the eedf through electron–electron (e–e) and electron–ion (e–i) Coulomb collisions. Moreover, in the arc case, thermal conditions are assumed, i.e., the same temperature for free electrons and heavy particles, and usually Maxwell (as already mentioned) and Boltzmann distributions for eedf and internal molecular states, respectively.[4]

Only recently has eedf in expanding arc conditions been studied. We have reported eedf for several measured excited state (metastable) concentrations of argon expanding in low-pressure flows.[5] The high concentration of free electrons in the flow smoothed the role of argon metastable states in altering the eedf, even though memory of the second-kind collisions from metastable argon was still present in the enhancement of the relevant rates.

The aim of this paper is to examine eedf in expanding atmospheric nitrogen arcs for the conditions studied by Laux et al.[4] These authors recently presented an experimental and numerical study on both the mechanism and amount of ionizational nonequilibrium created in recombining plasmas of air and nitrogen produced by a 50-kW rf plasma torch. Parts of their results are used in this paper to simulate initial conditions for our calculations, i.e., we solve an appropriate Boltzmann equation for eedf in the presence of realistic concentrations of electrons and in the presence of excited state concentrations exceeding the corresponding equilibrium ones.

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II. Boltzmann Equation

To reach our goal we solved a Boltzmann equation for the eedf written in the form[6]

$$\frac{\partial n(u, t)}{\partial t} = -\left(\frac{\partial J_{\mathrm{el}}}{\partial u}\right)_{e-N} - \left(\frac{\partial J_{\mathrm{el}}}{\partial u}\right)_{e-e} + In + Sup \qquad (1)$$

More detailed information about the terms in Eq. (1) can be found in Refs. 1 and 6.

The inelastic term includes the most important energy loss processes for rotation, vibration, and electronic excitation as well as for the ionization treated as an inelastic channel

$$In = In_{(\mathrm{rot})} + In_{(\mathrm{vib})} + In_{(\mathrm{electr})} + In_{(\mathrm{ion})} \qquad (2)$$

The rotational term was calculated according to the continuous approximation, whereas the vibrational term includes all transitions involving the first eight vibrational levels of nitrogen. Finally, the electronic term includes the most important excitation channels by electron impact for both radiative and metastable states.

The superelastic term describes the energy returned to free electrons from vibrationally and electronically excited states and, therefore, represents the source terms in the Boltzmann equation in the absence of an electric field (postdischarge conditions). In implicit from it can be written as

$$Sup = Sup_{(\mathrm{vib})} + Sup_{(\mathrm{electr})} \qquad (3a)$$

The first term represents the contribution from vibrationally excited molecules

$$e + \mathrm{N_2(v)} \rightarrow e + \mathrm{N_2(v')}, \qquad \mathrm{v} > \mathrm{v'} \qquad (3b)$$

whereas the second term includes the following channels:

$$e + \mathrm{N_2}(A^3\Sigma_u^+) \rightarrow e + \mathrm{N_2}(\mathrm{X}^1\Sigma_g) \qquad (3c)$$

$$e + \mathrm{N_2}(\mathrm{B}^3\Pi_g) \rightarrow e + \mathrm{N_2}(\mathrm{X}^1\Sigma_g) \qquad (3d)$$

$$e + \mathrm{N_2}(\mathrm{C}^3\Pi_u) \rightarrow e + \mathrm{N_2}(\mathrm{X}^1\Sigma_g) \qquad (3e)$$

These superelastic terms have been selected to cover the important regions of eedf: This selection is representative of inelastic processes, i.e., the reverse of processes Eqs. (3b–3e), with threshold energy less than 2 eV for vibration [Eq. (3b)] and of the order of 5, 7, and 11 eV for the three superelastic electronic terms [Eqs. (3c–3e)].

The superelastic terms entering the Boltzmann equation contain the population densities of the different excited states and the cross sections for second-kind collisions. This point can be understood by writing down one of the typical terms contributing to a superelastic expression. Let us consider for example the de-excitation of an excited state N_2^* by electron impact, i.e., the process

$$N_2^* + e(u) \rightarrow \mathrm{N_2} + e(u + u^*) \qquad (3f)$$

In this process electrons at energy u are heated through superelastic collisions at energy $(u + u^*)$, where u^* is the threshold energy of the process under consideration. The typical superelastic term therefore has the following form:

$$Sup = n_{N_2^*} n(u) \sigma^*(u) v(u) \qquad (4)$$

The superelastic cross section $\sigma^*(u)$ can be calculated from the corresponding inelastic cross section $\sigma_{\mathrm{in}}(u + u^*)$ applying the detailed balancing method, i.e.,

$$\sigma^*(u) = \sigma_{\mathrm{in}}(u + u^*)(u + u^*)/u g_0 / g^* \qquad (5)$$

where g_0 and g^* are the statistical weights of ground and excited states, respectively.

More information about the selected inelastic cross sections can be found in Ref. 6, where details about the discretization procedure used for solving the Boltzmann equation under stationary conditions, i.e., $\partial n(u, t)/\partial t = 0$ can also be found (also see Ref. 7–9).

III. Results

To solve the Boltzmann equation we need the concentrations of vibrationally and electronically excited states as well as the ionization degree and gas temperature in the expanding gas. As already mentioned, a realistic evaluation on part of these parameters (degree of ionization and gas temperature) can be done on the basis of experimental and numerical results reported in Ref. 4. On the other hand, the concentrations of vibrationally and electronically excited states have been assumed as free parameters.

In all of the cases studied the vibrational distribution has been considered as a Boltzmann one at a given vibrational temperature T_v that usually is considered equal to the gas temperature T_g. The concentrations of the three electronic states considered in the superelastic term, i.e., A, B, and C states, have been calculated from an equilibrium distribution at $T = T_v$ or by considering different overpopulations with respect to the thermal case. A sample of results has been reported in Figs. 1–5.

Figure 1 reports two eedfs calculated for typical thermal conditions; curve 1 refers to a complete thermal equilibrium at $T_v = T_g$, i.e., both vibrationally and electronically excited states are considered in equilibrium at $T_v = T_g = 5000$ K, whereas curve 2 considers vibrationally and electronically excited states in equilibrium at $T_v = 5000$ K and a slightly smaller translational temperature $T_g = 3000$ K. In both cases an ionization degree of 2×10^{-5} is considered. Keeping in mind that Maxwell eedfs vs energy in a semilog plot appear as straight lines, we can conclude that equilibrium eedfs are achieved when no overpopulation of excited states with respect to the equilibrium case is considered. In this case the role of e–e collisions and of reverse (equilibrated) processes in thermalizing eedfs are clearly evident. As a result the eedfs follow a Maxwell law at an electron temperature $T_e = 5000$ K.

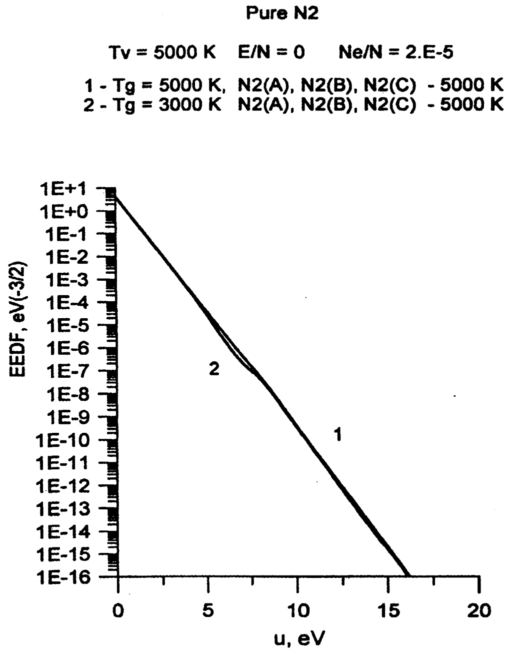

Fig. 1 Electron energy distribution functions vs energy for quasi-equilibrium conditions, calculation conditions are shown on the plot and in the text.

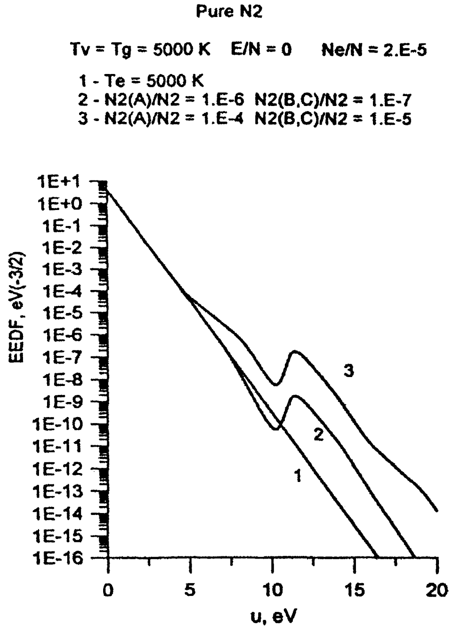

Fig. 2 Electron energy distribution functions vs energy for equilibrium (curve 1) and nonequilibrium conditions (curves 2 and 3), calculation conditions are shown on the plot and in the text.

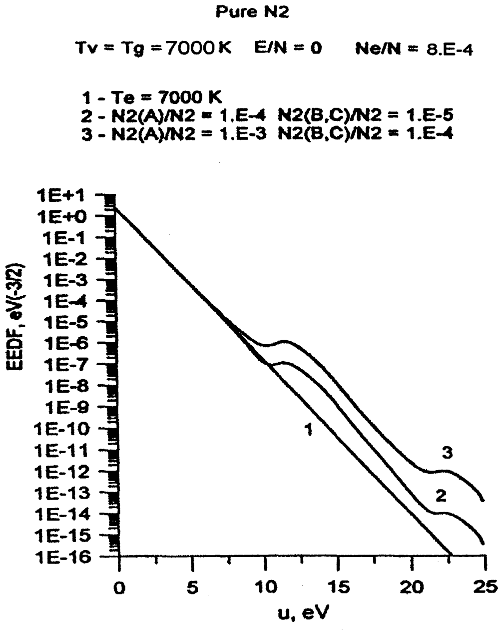

Fig. 3 Electron energy distribution functions vs energy for equilibrium (curve 1) and nonequilibrium conditions (curves 2 and 3), calculation conditions are shown on the plot and in the text.

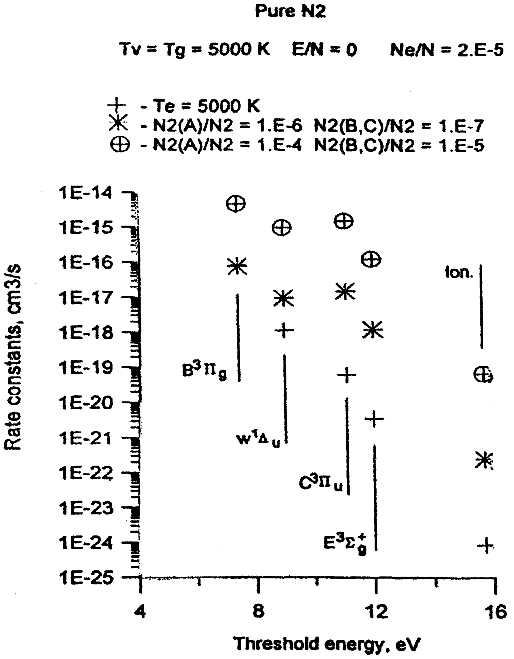

Fig. 4 Rate constants for inelastic processes as a function of threshold energy calculated according to different hypotheses on eedf, calculation conditions are shown on the plot and in the text.

Let us now consider different nonequilibrium situations. Figure 2 reports three eedfs calculated according to different hypotheses. Curve 1 is obtained by considering concentrations (molar fraction) of electronically excited states in equilibrium at $T_v = T_g = 5000$ K, whereas curves 2 and 3 have been obtained by considering concentrations of electronically excited states exceeding the equilibrium values. All of the cases described the vibrational distribution as a Boltzmann one at $T_v = T_g$. We can see that the presence of nonequilibrium concentrations of electronically excited states (curves 2 and 3) strongly enhances the eedf's tail compared to the equlibrium case (curve 1). The considered ionization degree is not sufficient to completely thermalize the eedf. The pronounced maximum at an energy u of approximately 11 eV is largely a result of the C state, whereas the role of A and B states is only apparent when the concentration of these states reaches a molar fraction of 10^{-4} and 10^{-5}, respectively (curve 3). Note also that curve 2 goes below curve 1 between 7 and 10 eV, this is most likely because of the prevalance of nonequilibrated inelastic losses.

Superelastic collisions play an important role in altering eedf, but only when the relative molar fraction of the electronically excited state is of the same order of magnitude as the molar fraction of electrons with energy equal to the electronic state threshold. This point can be understood by noting that the typical superelastic term [process e and Eq. (4)] should be compared to the corresponding inelastic term, i.e., the reverse of process e

$$In = n_{N_2}v(u + u^*)\sigma_{in}(u + u^*)n(u + u^*) \qquad (6)$$

This means that the effect of second-kind collisions is as high as the electron temperature T_e of the first part of eedf is small. This case increases the concentration of low-energy electrons that can be transported to higher energies through second-kind collisions. Moreover, because T_e is strongly coupled to T_v and T_g, the effects of second-kind collisions become very important when decreasing these last two temperatures; the reverse being true with increasing T_v and T_g. This last point is quite clear in Fig. 3, where we report other results obtained with different hypotheses on the concentrations of excited states, but assuming $T_v = T_g = 7000$ K. The effects in this case are strongly reduced compared with the corresponding ones in Fig. 2: In particular, the role of A and B states is completely canceled, whereas the role of the C state is well evident. It should be noted that the maximum at 11 eV reproduces itself at 22 eV as a result of the heating of the 11-eV electrons by the C state de-excitation.

Let us now consider how the differences in eedfs propagate into the different inelastic rate coefficients that can be calculated by integrating the relevant cross sections σ with eedf according to

$$\langle \text{rate} \rangle = \int_{u^*}^{\infty} u^*\sigma(u)f(u)u^{3/2}\,\mathrm{d}u \qquad (7)$$

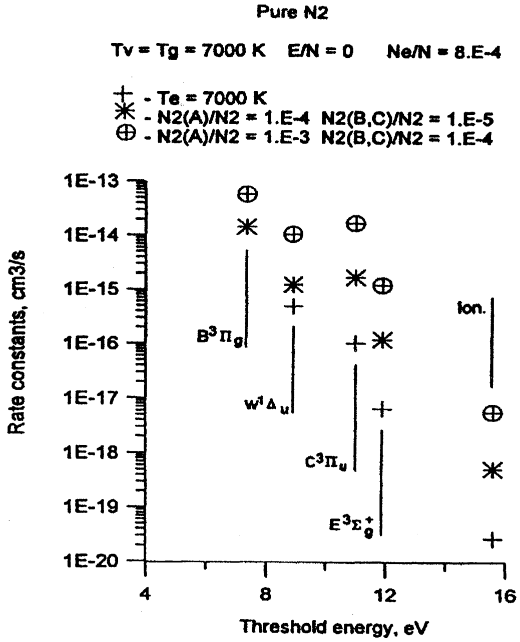

Fig. 5 Rate constants for inelastic processes as a function of threshold energy calculated according to different hypotheses on eedf, calculation conditions are shown on the plot and in the text.

The results calculated with eedfs of Figs. 2 and 3 have been respectively reported in Figs. 4 and 5. The rate coefficients have been plotted as a function of the threshold energy for selected processes (indicated in Figs. 4 and 5). The relevant rates depend on the considered eedf. In particular differences up to several orders of magnitude are observed depending on the concentrations of electronically excited states, these differences increasing as the threshold energy of the process rises. Let us consider as an example the rate coefficients corresponding to excitation of the $w^1\Delta_u$ state (threshold energy around 9 eV) and to ionization (threshold energy around 16 eV).

Figure 4 shows that the presence of electronically excited states increases the excitation rate of $w^1\Delta_u$ state by three orders of magnitude and the ionization rate as compared to the thermal conditions by five orders of magnitude.

These differences are strongly reduced when we consider situations at higher vibrational and translational temperatures (Fig. 5): In this case the differences in the excitation rate of the $w^1\Delta_u$ state are approximately within one order of magnitude, whereas large differences (up to three orders of magnitude) still persist in the ionization rates.

IV. Conclusions

The main conclusion of the present study is that in arc-expanding conditions structured eedfs can persist as a result of second-kind collisions. These structures can enhance the relevant rates by several orders of magnitude. This conclusion can be qualitatively considered independent of the selection of the particular states selected in this study. The results strongly depend on the concentration of excited states. In this connection we want to stress that case 3 of Fig. 2 strongly overestimates the concentration of the C state compared with the experiments of Ref. 4, so that the eedf in these experiments should be more Maxwellian than that predicted by the present study.

The present results must be considered as a first step toward the understanding of the possibility of nonthermal eedf under the so-called *thermal* conditions. The effect of this kind of nonequilibrium for recombining flows, such as that occurring under arc-expansion conditions, is still an open problem, the solution of which needs a more sophisticated model. Future work in this direction, certainly, should couple the Boltzmann equation for eedf to the kinetics of vibrationally and electronically excited states as done by our group for low-pressure, postdischarge conditions. In this way we will obtain actual concentrations of excited states. The self-consistent solution of the Boltzmann equations and the excited state kinetics approach should then be inserted in robust fluid dynamic codes to realistically describe the flow under strong nonequilibrium conditions. Attempts in this direction are presently in progress in different research groups.[8,9]

Acknowledgments

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