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Coupling of space-dependent electron dynamics and vibrational kinetics in radio-frequency discharges in nitrogen

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The coupling between the electron energy distribution function (EEDF) and the vibrational distribution in a parallel-plate radio-frequency discharge in low-pressure pure nitrogen is analyzed. A Monte Carlo electron dynamics is used assuming an imposed space- and time-dependent electric field, together with a space-dependent vibrational kinetics including nine vibrational levels of N_2 molecules. Calculations are performed for different deactivation frequencies of N_2 molecules. Space-dependent vibrational distributions, EEDF's, and rate coefficients are reported. It is found that the coupling with the vibrational kinetics can affect the results when the vibrational deactivation of molecules is mainly due to superelastic collisions with electrons.

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I. INTRODUCTION

Nitrogen discharges have been extensively studied in these last few years as a case study to show the coupling between the electron energy distribution function (EEDF) and excited-state kinetics. These studies deal with different conditions such as glow discharges [1], post discharges [2], and high-frequency bulk plasmas [3]. In all the studied conditions the importance of excited-state kinetics in shaping the EEDF has been shown.

On the other hand, a great deal of interest has been recently devoted to the study of EEDF's in radio-frequency sheath-dominated plasmas particularly emphasizing the role of electron dynamics on EEDF but neglecting the coupling between EEDF and nonlocal kinetics ("nonlocal" here means that, owing to free-electron diffusion, the rate coefficients cannot be written as a function of the local value of the reduced electric field E/p). Only recently the coupling of electron and chemical kinetics has been discussed in the framework of fluid models, that is at the macroscopic level [4,5]. A hybrid fluid Monte Carlo model including vibrational and chemical kinetics [6] has been also developed, but with a strongly simplified vibrational kinetics (only two vibrational levels for N_2) and without showing the effect of the coupling on the EEDF.

The aim of this work is to study the coupling between the nonlocal electron energy distribution function and the space-dependent vibrational distribution function in parallel-plate radio-frequency discharges in low-pressure nitrogen.

This coupling leads to two kinds of effects: the first one is the nonlocal pumping of the vibrational distribution function, and the second effect is the action of the excited vibrational levels of N_2 on the free-electron kinetics, leading to a reshaping of the electron energy distribution function.

In this work we emphasize that the cold-gas approximation (that is, the neglecting of excited species in the free-electron kinetics) cannot be used in plasma modeling without cautions, and suggest a criterion for a safe application of this approximation in space-dependent model of radio-frequency discharges in nitrogen.

II. DESCRIPTION OF THE MODEL

In our model the EEDF is calculated by performing a single-particle simulation of electron motion, including collision processes by the Monte Carlo method [7,8] and using an imposed space- and time-dependent electric field partially based on fluid model [9] calculations. The decoupling of field and dynamic problems was just considered by Kushner [10], but by using a different expression for the sheath field. With regard to the calculation of the free-flight time, the null-collision method [11,12] is used.

The equations of motion are solved by using the leapfrog method [8]. The space- and time-dependent electric field is made up of two contributions:

(1) The sheath field E_{sh},

$$E_{\mathrm{sh}} = -H(C\cos^2\pi ft - xC/l_s) + H(C\sin^2\pi ft - (d-x)C/l_s) \qquad (1)$$

which accounts for nonlocal heating of electrons in the strong sheath field.

(2) The bulk field,

$$E_b = -E_{0b}\cos 2\pi ft \ . \qquad (2)$$

Here H is a function defined as $H(\eta)=\max(0,\eta)$, x is the distance from one electrode, C is the peak value of the sheath electric field, l_s is the peak sheath length, f is the frequency, and d is the discharge gap.

The parameters l_s and E_{0b} are precalculated by using a local fluid model: local fluid models are not expected to give exact quantitative results in the operating conditions considered in this work, because the pressure is probably slightly too low, but exact quantitative results are not our concern here. Furthermore, this precalculation procedure saves the computational time otherwise necessary to couple electron dynamics and the Poisson equation.

After a value for E_{0b} has been selected, C is calculated in order to get the known applied radio-frequency voltage

$$V(t) = -V_{\mathrm{rf}} \cos 2\pi f t \qquad (3)$$

when integrating in the x coordinate the total electric field.

The following electron-molecule collision processes are introduced: elastic collisions of electrons with N_2 molecules in the ground and excited vibrational states, inelastic processes leading to rotational, vibrational (8 cross sections), and electronic (11 cross sections) excitation of N_2 from the ground state, and direct ionization of N_2 from the ground state. The set of cross sections used comes from Ref. [13]. The electronic excitation cross sections considered correspond to the following states and threshold energies: $A\,^3\Sigma$(6.17 eV), $B\,^3\Pi$(7.35 eV), $W\,^3\Delta$(7.36 eV), $B'\,^3\Sigma$(8.16 eV), $a'\,^1\Sigma$(8.40 eV), $a\,^1\Pi$(8.55 eV), $w\,^1\Delta$(8.89 eV), $C\,^3\Pi$(11.03 eV), $E\,^3\Sigma$(11.88 eV), $a''\,^1\Sigma$(12.25 eV), together with a lumped set of singlet states (13.0 eV). Cross sections for superelastic collisions of electrons with vibrationally excited N_2 molecules leading to the ground state are also included: these cross sections are calculated by using a detailed balance.

Anisotropic electron-molecule elastic scattering is taken into account by using the method of Ref. [14]. However, calculations performed assuming isotropic scattering and using the momentum transfer cross section [improved elastic scattering (IES)] show that inclusion of anisotropic scattering does not change significantly the results, probably because the discharge considered operates in a sufficiently collisional regime. This result confirms the validity of IES for these typical radio-frequency discharge conditions.

With regard to boundary conditions, we assume that if an electron hits one of the electrodes, it is simply reflected. We have tested that the calculated EEDF is only slightly affected by assuming different hypotheses concerning this point.

The electron motion is locally coupled with a vibrational kinetics for N_2 including 9 vibrational levels. The processes considered are vibrational excitation from the ground state and superelastic collision processes leading back to the ground state,

$$e + N_2(0) \leftrightarrow e + N_2(v)\ , \quad v = 1, \ldots, 8\ . \qquad (4)$$

We also consider a first-order deactivation process leading to the ground state,

$$N_2(v) \rightarrow N_2(0)\ . \qquad (5)$$

This last process represents in a phenomenological way both the wall impact deactivation of the vibrational excited states as well as other relaxation processes entering in the vibrational kinetics, such as V-T (vibration-translation energy transfer with molecules or atoms). The V-V processes (vibration-vibration energy transfer between molecules) have been neglected due to the low-pressure conditions considered in the present work.

The rate coefficient of a vibrational process of the kind (4) is given by

$$k = \int_0^\infty \sigma(\varepsilon) f(\varepsilon) (2/m_e)^{1/2} \varepsilon \, d\varepsilon\ , \qquad (6)$$

where $f(\varepsilon)$ is the electron energy distribution function (EEDF) of the free electrons, defined in such a way that the fraction of electrons with kinetic energy between ε and $\varepsilon + d\varepsilon$ is given by $f(\varepsilon)\varepsilon^{1/2} d\varepsilon$, $\sigma(\varepsilon)$ is the cross section for the corresponding elementary process, and m_e is the electron mass.

The coupling is realized by an iterative procedure because of the very different characteristic times of free electron and vibrational kinetics. No process for electron generation or destruction is included in the model, therefore the space-averaged value of electron concentration is an input for the model: it can be either obtained by probe measurements or calculated by using the fluid model.

In the present calculations there is no molecule diffusion included: this is a very strong simplifying assumption, but here we are interested only in observing essential effects due to vibrational kinetics. In any case, one must consider that the local kinetics are connected through free-electron diffusion, and this circumstance may reduce the gap between a real system and this model.

Some points should be underlined to get a proper position of this kind of model with respect to the literature. First of all, it is clear that this kind of model, being not self-consistent, would be considered far from the state of the art if seen from the point of view of modern particle-field modeling. At the same time, the vibrational kinetics of nitrogen used here is highly simplified with respect to the kinetics of standard use in the uniform case, in particular for the neglecting of cascade excitation starting from excited vibrational levels and for the use of a phenomenological deactivation leading directly to the ground state. Our model is an attempt to merge two wide but separate literatures concerning, from one side, the effects on electron kinetics due to a nonuniform electric field (self-consistent or not) in nonlocal conditions, and, from the other side, the effect of coupling of the electron kinetics with the internal state kinetics of the molecules in the gas mixture. The nonlocal kinetics of electrons has been intensively studied and presently it is very refined, up to and including self-consistent space-charge effects by particle in cell Monte Carlo collisions [8] (PIC-MCC) or hybrid fluid-particle models. However, such models are so highly time consuming that chemical kinetics has been, as a rule, neglected. The validity range of "state-of-the-art" particle models neglecting chemical kinetics is therefore open to question. On the other hand, an open question spontaneously arises when looking at the extraordinary wealth of effects predicted by numerical coupling of molecular vibroelectronic and electron kinetics in a uniform plasma simulation: which is the relevance of these effects for nonlocal, space-dependent systems? Our point of view is the following: the most urgent issue in exploring this new field is to observe the coupling of simple vibrational kinetics and a simple nonlocal electron dynamics. Our vibrational kinetics (neglecting many strictly vibrational processes, but, more seriously, also neglecting any electronic-vibrational state coupling and heavy species diffusion) and our electron dynamics (disregarding the self-consistent coupling with the space-charge field and probably oversimplifying boundary conditions for electrons) have been chosen accordingly for this point of view.

III. MODEL RESULTS AND DISCUSSION

In this section we show and discuss results of the model by assuming different values for the phenomenological deactivation frequency f_d.

We consider a parallel-plate radio-frequency reactor with a discharge gap of 3.6 cm, filled with nitrogen at a pressure of 100 mTorr. The peak applied voltage is 200 V. Local fluid model calculations [15] for this device give the values 0.3 V/cm and 1 cm for E_{0b} and l_s, respectively, and these values are used in the electron dynamics. An electron density of 4×10^9 cm^{-3} is assumed, based on experiments performed on a similar device [16]. The discharge gap is divided into nine slices as regards the coupling with vibrational kinetics.

Figure 1 reports the space-dependent stationary EEDF obtained assuming a value of 10 s^{-1} for the deactivation rate coefficient. This value for the deactivation rate coefficient is quite a low one, in the sense that in these conditions the vibrational distribution function is mainly controlled by the competition between inelastic and superelastic electron-molecule vibrational rate coefficients.

Also shown in Fig. 1 is the space-dependent EEDF calculated in the cold-gas approximation, i.e., without considering the effect of the presence of excited states. One can notice that there is a clear "hole" in the cold-gas EEDF in the energy range 2 eV$<e<$3 eV, produced by the effect of inelastic vibrational collisions. The hole is deeper in the center of the plasma, where the pumping effect of the sheath field is lower.

By inspecting, in Fig. 1, the EEDF consistent with the vibrational kinetics, one can see that the hole in the EEDF almost completely disappears because of the reduction of net electron energy losses when pumping up the vibrational distribution. This modification of the EEDF shape affects the values of the rate coefficients for processes having important cross sections in the electron energy range 2 eV$<e<$3 eV, the effect being higher in the center of the plasma. This is the case of the rate coefficients for the vibrational excitation of N_2.

In Fig. 2 the space-dependent rate coefficients for the vibrational excitation processes considered in the calculations are reported in two cases: (a) the cold-gas approximation, and (b) taking into account the vibrational kinetics. The rate coefficients shown in the figure have been weighted according to the spatial distribution of electrons. The weighted rate coefficient $k(x)$ is connected with the reaction rate R for a reaction of the kind (4) by the relation

$$R=k(x)[n][N_2(v,x)]\ , \tag{7}$$

where $[n]$ is the space-averaged electron concentration and $[N_2(v,x)]$ is the space-dependent concentration of species $N_2(v)$. It can be seen that the rate coefficients for vibrational excitation are affected by the vibrational kinetics, changing in the center of the plasma approximately by a factor of 2.

In Fig. 3 are reported the space-dependent coefficients for the electronic excitation of nitrogen molecules in the cold-gas approximation: the inclusion of a self-consistent vibrational kinetics has a negligible effect on the calculated values of these quantities, due to their high threshold energies.

Figure 4 reports the calculated space-dependent number densities of N_2 molecules in different vibrational states calculated assuming the values 10 and 100 s^{-1} for the phenomenological deactivation rate coefficient. By inspecting Fig. 4 it can be observed that, by increasing the deactivation frequency, the vibrational temperature not only decreases, but also becomes more sensible to the space profile of the electron density (that is, lower in the sheath regions).

This circumstance can be understood as follows.

(a) Both superelastic and inelastic vibrational processes are first-order processes with respect to electron concen-

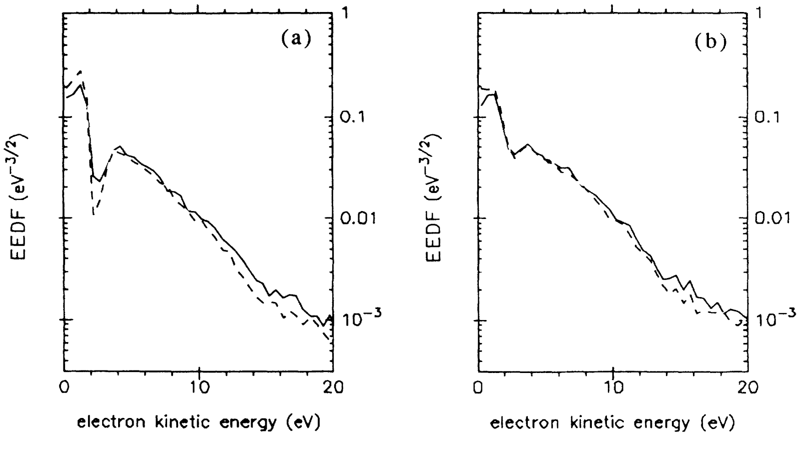

FIG. 1. Time-averaged EEDF at the position $x=0.167d$ (full line) and $x=0.5d$ (dashed line) calculated (a) disregarding the vibrational kinetics and (b) including it self-consistently with $f_d=10$ s^{-1}.

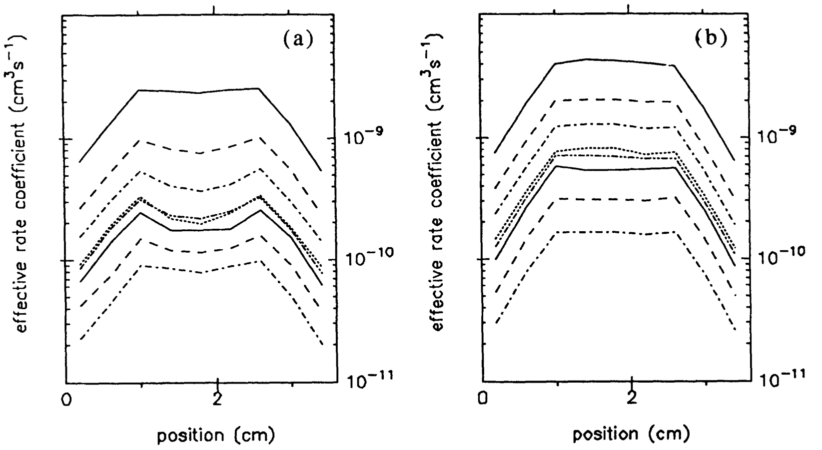

FIG. 2. Rate coefficients for vibrational excitation of N_2, calculated (a) disregarding and (b) taking into account the vibrational kinetics of N_2 with $f_d = 10$ s^{-1}. The upper line refers to the process $e + N_2(v=0) \leftrightarrow e + N_2(v=1)$, the lower one to the process $e + N_2(v=0) \leftrightarrow e + N_2(v=8)$. Intermediate lines from the top refer to $v = 2, \ldots, 7$, respectively.

tration, while the phenomenological deactivation is a zero-order process with respect to electron concentration.

(b) Inelastic and superelastic vibrational cross sections for lower vibrational levels are almost equal as a consequence of detailed balance principle, being peaked at significantly higher energy than the threshold one.

As a consequence, when inelastic and superelastic collisions with electrons compete to excite and deactivate N_2 molecules, the vibrational temperature can be very high and the electron density is inessential. On the contrary, when the competition is between inelastic collisions with electrons and zero-order deactivation, the vibrational temperature is controlled by the electron density.

The EEDF's calculated assuming $f_d = 100$ s^{-1} do not differ significantly from the one of Fig. 1(a), therefore we have not reported it. This last result shows that when the role of superelastic collisions in determining the vibrational distribution function is not important, the vibrational kinetics do not affect significantly the free-electron kinetics, and this last result can be studied using the cold-gas approximation.

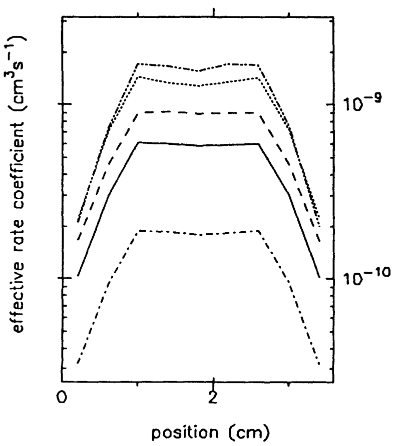

FIG. 3. Selected rate coefficients for electronic kinetics of N_2. The upper line refers to direct ionization from ground state, while the remaining four from the top to excitation of the states $C^3\Pi$, $B^3\Pi$, $A^3\Sigma$, and $a'^1\Sigma$, respectively.

Before ending this section we want to discuss how the present results can help to understand the experimental EEDF reported in Refs. [16] and [17]. Strictly speaking, Turner and Hopkins [17] were able to reproduce their experimental results by using a PIC-MCC model without considering excited-state kinetics. On the contrary, our results suggest that inclusion of a vibrational state kinetics can be at least help to understand the lack of the hole in the EEDF created by inelastic vibrational collisions. On the other hand, our results overestimate the tail of the EEDF compared to the experimental one. This point can be improved by a better description of the electric field as one by Turner and Hopkins. A phenomenological approach based on the introduction in our model of an ambipolar field [18] is able to reduce the tail of the EEDF. In this case the importance of superelastic vibrational collisions as well as superelastic electronic ones does increase indicating that the coupling of excited-state kinetics and the dynamics of free-electrons could play an important role under more realistic plasma conditions.

IV. CONCLUSIONS

In this work a model of a radio-frequency discharge in pure nitrogen at a *pd* value of 0.36 cm Torr is presented, which couples a single-particle Monte Carlo description of the free-electron dynamics with a one-dimensional vibrational kinetics of nitrogen.

A simplified space- and time-dependent electric field is assumed taking inspiration from fluid model results. Model runs have been performed assuming different values for a phenomenological vibrational deactivation rate coefficient. Results show that an important nonlocal pumping of the vibrational distribution function takes place in any case, but with basically different behaviors depending on whether molecule collisions with the wall or superelastic collisions with electrons control the amount of vibrational excitation.

When the second circumstance occurs, a description of the free-electron dynamics disregarding superelastic collisions of electrons with molecules is unable to give the correct electron energy distribution function and vibrational excitation rate coefficients, despite the strong pumping effect of the oscillating sheath field, and a self-

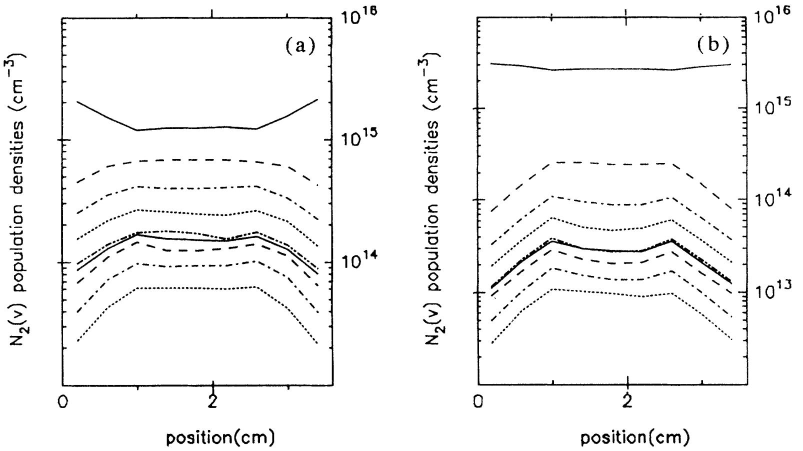

FIG. 4. Space-dependent populations of vibrational states of N_2, calculated with (a) $f_d = 10\ s^{-1}$ and (b) $f_d = 100\ s^{-1}$. The upper line refers to $N_2(v=0)$, the lower one to $N_2(v=8)$. Intermediate lines from the top refer to $v = 2, \ldots, 7$, respectively.

consistent approach including a vibrational kinetics of nitrogen must be used, in an analogous way to zero-dimensional models.

It turns out that while a local-field approximation for the calculation of the rate coefficients of chemical kinetics in low-pressure radio-frequency discharges in nitrogen is not applicable in general, one could disregard the effect of the vibrational kinetics on the EEDF when it is controlled mainly by deactivation mechanisms not involving free electrons. Extension of the present considerations to PIC-MCC models and to other molecular gases is favorable in order to establish the validity range of the classical simplified approach to radio-frequency discharge modeling.

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