Features of the formation of the distribution function of fast electrons formed in plasma as a result of processes involving metastable atoms and molecules

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The analysis of the influence of Penning ionization and de-excitation processes involving long-lived metastable atoms and molecules on the formation of electron distribution functions in gas-discharge plasma with recombination nonequilibrium is performed and their classification is given.

Keywords: Penning ionization, de-excitation, long-lived metastable atoms and molecules, electron distribution function.

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Concentration n_m of long-lived metastable atoms and molecules in gas-discharge plasma is usually comparable to or exceeds the concentration of charged particles ($n_m > n_e$), and their excitation energies E_m are significantly higher than the electron temperature ($E_m > T_e$; see, e.g., [1] for more details). Therefore, the reservoir of potential energy stored in metastable particles is normally significantly greater than the energy of electron gas: $E_m n_m > n_e T_e$. The release of even a fraction of this energy into free electrons may affect significantly their distribution function and other plasma parameters.

The primary channels of transformation of potential energy A_m of metastable particles into the kinetic energy of electrons are the processes of Penning and associative ionization

$$A_m + A_m(A) \rightarrow A^+(A_2^+) + A + e(E_p) \qquad (1)$$

and de-excitation of metastable particles in their collisions with slow (thermal) electrons

$$A_m + e \rightarrow A + e(E_m). \qquad (2)$$

It can be seen from (2) that the de-excitation process of interest to us dominates over the reverse excitation process only when the concentration of metastable levels is higher than the equilibrium (Boltzmann) concentration. This yields a limit on electron temperature in such plasmas with recombination nonequilibrium ($g_{a,m}$ are the statistical weights of the ground and metastable levels and n_a is the concentration of normal atoms):

$$T_e < E_m/\big(\ln(g_m n_a/g_a n_m)\big). \qquad (3)$$

It has been demonstrated in numerous experiments that, although the electron spectra of reactions (1), (2) are narrow peaks near the energy of their appearance (E_p, E_m), the contribution of reactions (1), (2) may be manifested in the electron distribution function (EDF) in plasma itself both in the form of peaks reproducing the shape of sources and in the form of a continuous spectrum („step“) at energies lower than the appearance one (E_p, E_m) (see the figure; a more detailed description is given, e.g., in [1]).

Since the energy of fast electrons emitted as a result of reactions (1), (2) exceeds significantly the temperature of electrons of the main group, they will heat the latter in collisions with them, thus affecting the constants of the processes of stepwise excitation and ionization. This effect is the most profound in the case of step-type EDFs (when fast electrons relax in collisions in the bulk [1]). In turn, the method of plasma electron spectroscopy (PLES), which is used for analysis of impurities in gases, is based on the recording of EDF peaks and, consequently, the energy of produced electrons [1,2]. Therefore, the question of the type of distribution function of fast electrons emitted as a result of reactions (1), (2) remains relevant.

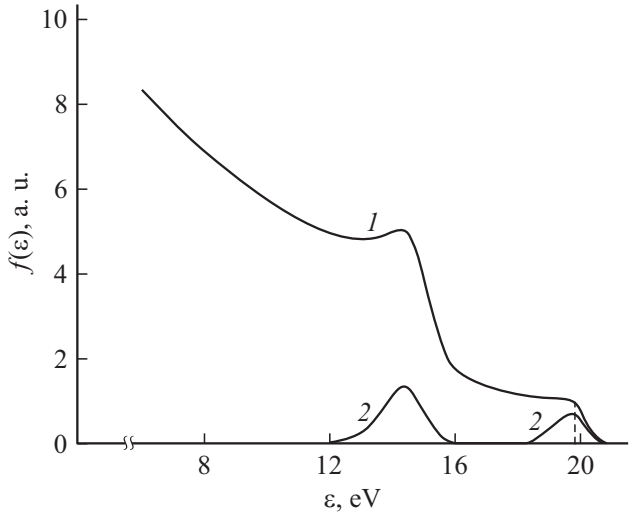
In the present study, the formation of EDFs as a result of reactions (1), (2) in gas-discharge plasma is analyzed, and their classification is provided. It is demonstrated that various combinations of the two limiting cases (peaks or steps) indicated above may be obtained under different conditions.

Since electrons emitted as a result of reactions (1), (2) are „external“ with respect to plasma electrons, the EDF in this plasma may be presented as sum $f_0 = f_{0s} + f_{0f}$, where f_{0s} is the distribution function of plasma electrons and f_{0f} is the distribution function of electrons emitted as a result of reactions (1), (2) [1].

In most practically relevant cases, the distribution function of plasma electrons up to the threshold of inelastic processes ($\varepsilon \leqslant \varepsilon^*$) may be approximated by an exponential (Maxwellian) function with effective temperature T_e [1]:

$$f_{0s}(\varepsilon, r) = \big(2/T_e^{3/2}\sqrt{\pi}\big) n_e(r) \exp(-\varepsilon/T_e). \qquad (4)$$

As is known, it is impossible to obtain a general analytical solution of the Boltzmann equation in both energy and



Two limiting cases of distribution of fast electrons emitted as a result of reactions (1), (2) in the afterglow of helium [1]. *1* — Step; pressure $p = 7.6$ Torr, and the delay time after a current pulse with an amplitude of 100 mA was 70 μs. *2* — Peaks near energies $E_p = 14.5$ eV, $E_m = 19.8$ eV; pressure $p = 0.3$ Torr, and the delay time after a current pulse with an amplitude of 190 mA was 120 μs.

coordinate variables; therefore, two main approximations are used in practice to find f_{0f}.

These are the traditional local approximation, where all spatial gradients are neglected in the kinetic equation, and the opposite Holstein–Tsendin approximation of complete nonlocality, where terms with spatial transport dominate over collisional relaxation in the bulk.

The implementation of these two limiting cases is governed by relaxation parameter k, which is the ratio of rates of collisional processes in the bulk and the spatial transfer of electrons to plasma boundaries [1]. This parameter may be estimated by comparing the corresponding terms in the Boltzmann kinetic equation for electrons.

It should be taken into account that collisions of electrons with heavy particles may be divided into two main types according to energy loss.

Collisions of the first type are elastic (quasi-elastic) with a small energy change in a single collision ($\delta = 2m/M \ll 1$, where m is the mass of an electron and M is the mass of an atom). The corresponding rate of energy loss $\delta\nu$ is δ times lower than rate ν of elastic scattering of electrons. In molecular gases, these quasi-elastic processes with low energy loss are collisions of electrons with rotational and vibrational levels of molecules ($\Delta E_r, \Delta E_\nu \ll E_p$). The second type includes inelastic processes of excitation and ionization of electronic states of atoms and molecules, wherein an electron loses all excitation energy E_m in a single collision (ν^* is the inelastic collision rate).

In the „elastic“ energy region ($\varepsilon < \varepsilon^*$, ε^* is the excitation threshold), relaxation parameter $k = \delta\nu\tau = L^2/\lambda_\varepsilon^2$. Here, $\tau = L^2/D_r$ is the time of free diffusion of electrons to the boundaries, L is the characteristic size of a plasma region, and $\lambda_\varepsilon = \lambda/\sqrt{\delta} > 100\lambda$ is the energy relaxation length of electrons in the „elastic“ energy region (λ is the mean free path).

Accordingly, in the „inelastic“ energy region ($\varepsilon > \varepsilon^*$), parameter $k^* = \nu^*\tau = L^2/\lambda_\varepsilon^{*2}$, where $\lambda_\varepsilon^* = \sqrt{\lambda\lambda^*}$ is the energy relaxation length of electrons in the „inelastic“ energy region. Since $\nu^* \gg \delta\nu$, we have $k^* \gg k (\lambda_\varepsilon^* \ll \lambda_\varepsilon)$.

Since electrons in reactions (1) and (2) fall into the „elastic“ and „inelastic“ energy regions, respectively, it is convenient to examine the EDF formation in reactions (1), (2) separately.

1. EDF in the case of reaction (2) of de-excitation of metastable levels. In the local regime of EDF formation with parameter $k^* > 1 (L > \lambda_\varepsilon^*)$, the EDF corresponding to reaction (2) is determined by the balance of direct and reverse processes of excitation and de-excitation of a metastable level by thermal electrons with subsequent rapid re-excitation. Therefore, the EDF in this case is the distribution function of thermal electrons (shifted by the excitation threshold) with a ratio of concentrations of metastable particles and neutral gas $\sim n_m/n_a$:

$$f_{0f}(\varepsilon, r) = n_e(r)(g_0/g_m)(n_m/n_a)(r) \times \left(2/T_e^{3/2}\sqrt{\pi}\right) \exp\left(-(\varepsilon - \varepsilon^*)/T_e\right). \quad (5)$$

Since $\varepsilon^* \gg T_e$, EDF (5) actually assumes the shape of a peak with width $\sim T_e$ near excitation energy ε^*.

In the opposite nonlocal case ($k^* < 1$, $\lambda_\varepsilon^* > L$), fast electrons emitted as a result of reaction (2) have no time to undergo inelastic excitation before reaching the walls. The typical values of elastic ($\sim 10^{-15}$–10^{-16} cm^2) and inelastic ($\sim 10^{-16}$–10^{-17} cm^2) scattering cross sections yield an estimate of the conditions under which this regime is observed: $pL < 0.1$–1 cm · Torr. The EDF is determined in this case by the balance of production in reaction (2) and diffusion annihilation at the walls [1]:

$$f_{0f}(\varepsilon, r) = n_e(r)(g_0/g_m)(n_m/n_a)(r)\left(2/T_e^{3/2}\sqrt{\pi}\right) \times \exp\left(-(\varepsilon - \varepsilon^*)/T_e\right)\nu^*(\varepsilon)\tau(\varepsilon). \quad (6)$$

It is evident that this EDF is also represented by a peak near the excitation energy with width $\sim T_e$ and a $(k^* = \nu^*\tau < 1)$-fold difference in absolute value.

Thus, in both local and nonlocal regimes, the EDF corresponding to reaction (2) is a peak with a width on the order of the thermal electron temperature.

2. EDF in the case of Penning ionization involving metastable particles (1). Since the „elastic“ region is characterized by $k < k^* (\lambda_\varepsilon > \lambda_\varepsilon^*)$, the conditions of implementation of the local regime ($k > 1$, $\lambda_\varepsilon < L$) are more stringent than in the „inelastic“ energy region. In this case, electrons emitted as a result of reaction (1) relax in elastic collisions with a small energy loss in a single collision

($\delta \ll 1$), having no time to diffuse to the boundaries of the plasma region. Therefore, the corresponding EDF is governed by the energy degradation of electrons in quasi-elastic collisions with low energy loss. As a result, the EDF corresponding to reaction (1) is a continuous spectrum (step) extending from energy E_p of appearance of fast electrons toward lower energies [1]:

$$f_{0f}(\varepsilon, r) = \beta_m n_m^2(r)/\left(\varepsilon^{3/2}(\nu_e + \delta\nu)\right), \quad \varepsilon < E_p. \qquad (7)$$

In (7), β_m is the constant of process (1) and ν_e is the electron–electron collision rate.

The corresponding estimate of concentration of fast electrons emitted as a result of reaction (1) is $n_{ef}(r) \sim \beta_m n_m^2(r)/(\nu_e + \delta\nu)$.

In the other limiting case (low pressures), when $k < 1$, $\lambda_\varepsilon > L$ (nonlocal regime) in the „elastic“ energy region, the terms with spatial transfer of electrons in the Boltzmann kinetic equation dominate over the change in their energy due to elastic collisions in the bulk. Although the entire plasma volume is accessible to nonlocal electrons, the issue of their propagation to the walls with subsequent annihilation is decided by wall potential $e\Phi_w$ (the potential difference between the tube axis and the wall).

Since nonlocal electrons cross the discharge volume faster than they change their energy due to collisions, the entire ensemble of nonlocal electrons is divided into two essentially different groups: (1) thermal electrons with energy $\varepsilon < e\Phi_w$ that are trapped in the bulk, cannot escape to the walls, and set electron concentration n_e; (2) transient electrons with $\varepsilon > e\Phi_w$ that reach the plasma boundaries in the free diffusion regime, ensuring the equality of electron and ion fluxes to the walls.

At the considered low temperatures, the energy of appearance of fast electrons as a result of reactions (1), (2) $E_p > e\Phi_w$, and these electrons propagate to the walls in the free diffusion regime. Thus, as in the above-discussed case (6), the EDF is determined by the balance of production in reaction (1) and diffusion annihilation at the walls. Consequently, the nonlocal EDF corresponding to reaction (1) reproduces the shape of their source $R(\varepsilon)$ in the form of a peak at appearance energy E_p:

$$f_{0f}(\varepsilon, r) = \beta_m n_m^2(r) R(\varepsilon)\tau. \qquad (8)$$

In (8), $R(\varepsilon)$ is the normalized ($\int_0^\infty R(\varepsilon)\sqrt{\varepsilon}d\varepsilon = 1$) spectrum of reaction (1) that assumes the shape of a narrow peak with a width of ~ 1 eV near energy E_p.

However, the above-discussed scenario of non-local EDF (8) formation is disrupted at relatively high concentrations of metastable particles ($n_m/n_e \gg 1$). In this case, the flux of fast electrons emitted as a result of reactions (1), (2) in the free diffusion regime may exceed the flux of ambipolar diffusion of ions (characteristic time τ_{amb}); i.e., the following condition may be satisfied: $\beta_m n_m^2 > n_e/\tau_{amb}$.

A curious phenomenon of self-blocking of a fraction of fast electrons needed to maintain quasi-neutrality and equalize the fluxes of electrons and ions to the walls then arises [1]. The near-wall potential jump, which blocks a fraction of the fast electron flux and equalizes the fluxes of ions and electrons to the walls, becomes equal to E_p. A part of the EDF then transforms from a peak into a step, which may be estimated as

$$f_{0f}(\varepsilon, r) \approx \left(\beta_m n_m^2(r) - n_e/\tau_{amb}\right)/\left(\varepsilon^{3/2}(\nu_e + \delta\nu)\right), \varepsilon < E_p, \qquad (9a)$$

while the remaining part of the fast electron flux goes to the wall

$$f_{0f}(\varepsilon, r) \approx (n_e/\tau_{amb}) R(\varepsilon)\tau, \qquad \varepsilon > E_p. \qquad (9b)$$

Thus, it follows from our analysis that various combinations of the two key limiting cases (peaks or steps) may be obtained under different conditions. Accordingly, reactions (1), (2) will have a different effect on the plasma parameters. Let us illustrate this with two typical examples.

1. A single EDF of the entire ensemble of electrons with a certain temperature (average energy) is assumed in the most commonly used computational codes for self-consistent simulations of gas discharges within the hydrodynamic (fluid) approximation [3,4]. In this scenario, all the energy of fast electrons produced in reactions (1), (2) is automatically contained in a single ensemble of electron gas. In turn, the contribution of reactions (1), (2) in the electron energy balance equation is written as $Q_{heat} = \beta_m n_m^2 E_p + \beta_e n_m n_e E_m$ [3,4]. Therefore, the electron temperature determined this way may be overestimated (especially in the nonlocal regime, where heating of electrons of the main group emitted as a result of reactions (1), (2) is virtually lacking).

2. The formation of EDF peaks with the energy of appearance of fast electrons, which are emitted as a result of reaction (1) of Penning ionization of metastable particles of the main gas A_m with impurities $B\left(A_m + B \rightarrow B^+ + A + e(E_{mix})\right)$, makes it possible to determine impurity ionization potential $E_i = E_m - E_{mix}$ based on the measured energy of fast electrons and identify this impurity. This forms the basis of PLES analysis of gases [1,2]. Therefore, the criteria for observation of EDFs in the form of peaks obtained in the present study are important for correct application of this method in practice. In turn, it is hard to apply PLES analysis to step-type EDFs, and further studies are needed in this case.

It should also be noted that one needs to solve the full Boltzmann kinetic equation in both energy and coordinate variables to find the EDF in cases intermediate between the considered limiting ones ($k \ll 1$ and $k \gg 1$).

Conflict of interest

The authors declare that they have no conflict of interest.

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