A Study of the Motion of High-Energy Electrons in a Helium Hollow Cathode Discharge

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The motion of high-energy electrons was studied in a helium hollow cathode discharge using Monte Carlo simulation. The calculations were carried out in the pressure range of 2–10 mbar. The length of the cathode dark space (CDS) was determined by simulation in an iterative way using experimental voltage-current density characteristics of the discharge. At the lowest helium pressure (2 mbar) the concentration of high-energy electrons was found to be the same at the CDS-negative glow boundary and at the midplane of the discharge while at 8 mbars it was found to be by 1–2 orders of magnitude smaller. The results of our calculations support the existence of "oscillating" electrons. The probability of 1, 2 and 3 transfers through the negative glow (NG) for primary electrons was found to be 37%, 11% and 2%, respectively, at 2 mbar pressure. The spatial distribution of ionizations and the angular distribution of electron velocity at the CDS-NG boundary were also investigated. The pressure dependence of the current balance at the cathode was obtained, and the results indicate that with decreasing pressure other secondary emission processes than ion impact become important in the maintenance of the discharge.

Key words: Hollow cathode discharge, Electron energy distribution, Monte Carlo simulation, Oscillating electrons, Current balance.

1. Introduction

The properties of (cold cathode) hollow cathode (HC) glow discharges have been examined for a long time [1–7]. The main uses of this type of discharges are hollow cathode light sources [8, 9] and gas lasers [10–13].

The hollow cathode effect occurs when for example the separation of two parallel plane cathodes is decreased from a large distance and the separate negative glows start to coalesce. If a fixed voltage is applied, the discharge current may rise orders of magnitude compared to the "normal" current in a single plane cathode discharge.

According to [14] three different phenomena contribute to the hollow cathode effect:

- because of the cathode geometry photons and metastable atoms can reach the cathode with a higher probability and release more electrons than in an ordinary discharge,
- as proposed by Güntherschulze [15], there may exist so-called "pendelelectrons" which oscillate between the opposite cathode surfaces and increase the ionization and excitation rate [16],
- due to the increased concentration of excited and charged species in the negative glow additional processes (the rates of which depend nonlinearly on the concentrations) may become significant and increase further the current at constant voltage.

The first experimental evidence of the existence of oscillating electrons was given by Helm [14] who observed electrons at the cathode emitted from a probe on the opposite side of a cylindrical hollow cathode.

Those electrons emitted from one of the cathodes and reaching the "opposite" cathode surface have the same energy distribution as the primary ones. These slow electrons have a great chance to get absorbed by the cathode [17]. At low pressures this effect causes a significant loss in the ionization rate and limits the lowest possible operating pressure of the HC discharge [14].

In ordinary plane cathode discharges the role of ultraviolet (UV) photons in the maintenance of the discharge was found to be relatively unimportant [18]. On the other hand, in HC discharges the high importance of photoelectrons emitted by the cathode due to UV radiation from the discharge has been experimentally demonstrated [19, 20].

Much work has been devoted to the study of the cathode region of glow discharges in ordinary plane and hollow cathode geometries [3–7, 21–29]. This

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paper reports on our investigations on hollow cathode (HC) discharges aiming to get detailed information on the motion of electrons. Our calculations were based on Monte Carlo simulation. The length of the cathode dark space (CDS) was obtained using measured voltage-current density characteristics of the discharge. The electron energy distribution function (EEDF) at the CDS-negative glow (NG) boundary and at the midplane of the discharge was calculated at different pressures. The probability of multiple transfers through the NG for primary electrons was determined in order to see whether there exist "oscillating" electrons in the discharge. The spatial distribution of ionizations, the angular distribution of electrons at the CDS-NG boundary were also investigated as well, as the pressure dependence of the current balance at the cathode. In the calculations we used a fixed cathode separation $L = 1$ cm and carried out calculations in the $p = 2$ to 10 mbar pressure range.

2. The Model of the Discharge

The discharge geometry and the electric field distribution considered in the model are shown in Figure 1. The cathodes of the discharge (C1 and C2) are round shaped having a radius R and they are placed parallel

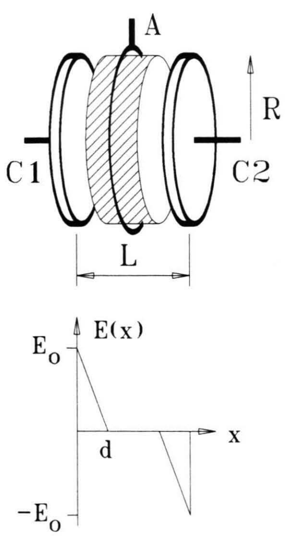

Fig. 1. The hollow cathode discharge geometry used in the calculations and the specified $E(x)$ electric field distribution. (C1 and C2: cathodes, A: anode, L: the distance between the cathodes, R: radius of the cathodes, dashed region: negative glow, d: the length of the CDS).

to each other at a distance L. The anode (A) is placed around the negative glow region at $L/2$ distance from the cathodes. In the model the $2R \gg L$ case is considered, i.e. edge effects are ignored.

The motion of electrons in the HC was described by Monte Carlo simulation.

The electric field distribution (see Fig. 1) is specified *a priori* based on experimental investigations [1]. In the CDS a linearly decreasing electric field distribution was applied. The electric field at the CDS-NG boundary was supposed to be 5 eV/cm. This small residual field does not modify the results of the calculation significantly but the zero field position must be excluded from the CDS because of the applied Monte Carlo procedure [22]. The negative glow was supposed to be free of electric field [1].

Recent experimental investigations pointed out that the number of ions entering the CDS from the NG is small compared to the number of those created in the CDS [30, 24]. In the model we assume that no ions enter the CDS from the NG.

The elementary collision processes considered in the model are anisotrope elastic electron scattering, electronic excitation, and electron impact ionization.

2.1. The Method of the Simulation

In the algorithm of simulation the electrons are released one by one from one of the cathodes (C1, see Figure 1). The motion of the emitted electrons and all additional electrons created in ionizing collisions are traced by the CDS and NG Monte Carlo procedures. The CDS Monte Carlo procedure is based on the work of Boeuf and Marode [22], the NG Monte Carlo procedure is simpler because the NG is supposed to be free of electric field. In these procedures the distance between successive collisions of electrons is determined by random numbers. The accelerating effect of the electric field (in the CDS) and the energy dependence of collision cross sections are taken into account. In the CDS simulation procedure the null-collision method is applied to speed-up the computation [31, 22].

The electrons are traced until they leave the CDS or their kinetic energy falls below the ionization potential of helium ($E_i = 24.56$ eV) in the NG. The low energy electrons are trapped in the negative glow and do not contribute to direct electron impact ionization. They may participate in excitation, cumulative ionization processes (not considered in the model) and carry the current to the anode.

Although the electric field is one dimensional, the electrons move in a three dimensional space. The state of an electron in the phase space is characterized by its position (x), energy (ε) and cosine (μ) of the angle θ measured between the x-axis and the electron's velocity vector (as in [22]).

The cross sections of the considered elementary processes are taken from [32] and [33]. In the case of elastic scattering the scattering angle is determined randomly considering the form of the differential cross section of the process used by Boeuf and Marode [22]. The scattering after excitation is assumed to be isotropic, the scattering angle is chosen randomly, as well as the energy loss of the electron. In the ionization process the scattered and ejected electrons share the remaining kinetic energy and the directions of their velocity vectors are assumed to be coplanar and perpendicular [22].

The electrons are emitted from the cathode with an initial energy randomly distributed between zero and $(E_i - 2E_0)$ eV, where E_i and E_0 are the ionization potential of He and the work function of the cathode material, respectively [34].

In the simulation the electrons may be absorbed by or reflected from any of the two cathodes, the reflection coefficient was taken to be 0.2 [17].

In the simulation only the half of the HC discharge is considered. Because of the symmetry, whenever an electron crosses the midplane of the HC, another electron is supposed to arrive from the other side with the same energy and oppositely directed velocity.

While tracing the electrons the electron energy distribution function (EEDF) builds up at given positions in the discharge region [22]. Also the fluxes of electrons and He^+ ions per emitted electron are obtained in the CDS. These quantities already make it possible to calculate the current density as it is shown in some detail in the following.

2.2. Calculation of the Discharge Parameters

Our primary aim is to be able to calculate the current density from the given voltage and the results of the simulation.

The $v^+(x)$ average velocity of He^+ ions in the CDS is given by

$$v^+(x) = \sqrt{\frac{2e\,E(x)}{\pi n M \sigma_s}}\,, \tag{1}$$

where e is the electronic charge, n the He concentration, M the He^+ ion mass and σ_s the cross section of the $He^+ + He \rightarrow He + He^+$ symmetric charge transfer process [24]. The cross section σ_s depends, however, on the $\varepsilon = M(v^+)^2/2$ kinetic energy of the ion as [35–37]

$$\sigma_s = k_1 - k_2 \cdot \ln(\varepsilon)\,, \tag{2}$$

where k_1 and k_2 can be considered to be constants within the ion velocity range of interest and are known from experimental investigations [37]. The average ion velocity v^+ is calculated by the iterative solution of (1) and (2).

From the MC simulation we obtain the fluxes of electrons and He^+ ions per emitted electron: $F^-(x)$ and $F^+(x)$. The current density consist of electron and ion current densities and $j = j^-(x) + j^+(x)$ holds in the stationary case. Moreover we can define $\phi(x)$ as

$$\phi(x) = \frac{j^+(x)}{j} = \frac{F^+(x)}{F^+(x) + F^-(x)}\,. \tag{3}$$

Since the positive space charge (created by He^+ ions) is dominant in the CDS the Poisson equation may be written:

$$\frac{\mathrm{d}E(x)}{\mathrm{d}x} = -\frac{1}{\varepsilon_0}\,\varrho^+(x)\,, \tag{4}$$

where ϱ^+ is the positive space charge $\varrho^+(x) = j^+(x)/v^+(x)$. Using the boundary condition that the electric field at the CDS-NG boundary is, $E(x=d) \cong 0$ the electric field distribution in the CDS is obtained by integration of (4):

$$E(x) = -\frac{1}{\varepsilon_0}\int_d^x \varrho^+(\xi)\,\mathrm{d}\xi = -\frac{1}{\varepsilon_0}\,j\int_d^x \frac{\phi(\xi)\,\mathrm{d}\xi}{v^+(\xi)}\,. \tag{5}$$

Furthermore the discharge voltage is:

$$V = \int_0^d E(x)\,\mathrm{d}x = -\frac{1}{\varepsilon_0}\,j\int_0^d\int_d^x \frac{\phi(\xi)\,\mathrm{d}\xi}{v^+(\xi)}\,\mathrm{d}x\,, \tag{6}$$

from which the discharge current density j can be calculated.

This calculation is straightforward if d, the length of the CDS is known (e.g. from experiments). When d is only approximately known and the $j(V)$ characteristics of the discharge are measured, d may be determined in an iterative way. The simulation is carried out using the same voltage and pressure values as in the experiment, and d is adjusted in the consecutive

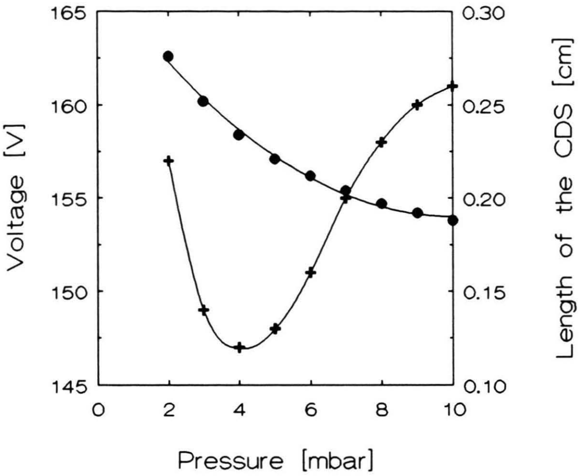

Fig. 2. The measured $V(p)$ characteristics of the discharge (+) at constant $j = 1$ mA/cm^2 and the length of the CDS (•) as a function of p.

runs to result in a current density in agreement with the measured value. In our calculations the latter method was chosen.

3. Experimental

Because of the lack of experimental data on d in hollow cathode discharges an experiment was carried out to obtain the voltage-current density [$V(j)$] characteristics of the discharge. In order to keep the gas relatively cool the $V(j)$ characteristics of the discharge were recorded in pulsed operation and using the averaging mode on a HP 54501 A digitizing oscilloscope.

The experimental discharge tube consisted of 48.5 mm diameter round faced electrodes placed 10 mm apart serving as cathodes. The anode was a circle shaped wire of about 52 mm diameter placed at half distance between the electrodes. The cathode material was high purity aluminium.

The measured discharge voltage (obtained from the $V(j)$ curves) as a function of He pressure is shown in Fig. 2 at a constant current density of 1 mA/cm^2. Starting from 10 mbar pressure the voltage decreases towards lower pressures. It can be seen that the lowest voltage representing the best operating conditions for the HC discharge occurs at $p = 4$ mbar. At even lower pressures the voltage increases rapidly. The pressure dependence of the length of the CDS (calculated in the iterative manner explained in 2.2) is also plotted in Figure 2.

4. Results and Discussion

In the following, results obtained from the calculations are presented.

In Figs. 3 and 4 the EEDF is shown at 2 and 8 mbar pressures at $x = d$ (CDS-NG boundary) and at $x = L/2$ (midplane of the discharge). The peak in the EEDF at the highest electron energies represents the beam electrons. The shape of these peaks is identical to the initial energy distribution of primary electrons. Figure 3 indicates that the density of beam electrons at the CDS-NG boundary at 8 mbar pressure is by one order of magnitude smaller than that at 2 mbar. At the midplane of the discharge this ratio is about 1/100. It can also be noticed that the beam electron density at $x = d$ and at $x = L/2$ is about the same at 2 mbar. Contrary to this, the beam electron density decreases by about an order of magnitude from the boundary to the middle of the discharge at 8 mbar pressure.

The primary electrons emitted from the cathode are accelerated in the CDS and may cross the negative glow once or several times. Figure 5 shows the pressure dependence of the probability that a primary electron crosses the NG once, twice and three times. It can be seen in Fig. 5 that at the lowest pressure (2 mbar) about 37% of the primary electrons emitted from the "left" cathode fly into the opposite ("right") CDS, $\approx 11\%$ comes back to the "left" CDS and $\approx 2\%$ crosses the NG once more. The probabilities of the given numbers of transfers fall closely exponentially as the pressure increases. It is noted that at the "optimal pressure" (at the lowest operating voltage) only $\sim 9\%$ of the primary electrons cross the NG and the probability of multiple transfers is rather small.

The angular distribution of the electron's motion at a given $x = x_0$ plane can be visualized by storing the ε and μ values for each electron crossing the $x = x_0$ plane and plotting the stored values as dots on the (ε, μ) phase plane. Also the axial v_x and radial v_R components of the velocity instead of ε and μ may be used. (v_x and v_R are related to the ε and μ variables as $v_x = v \cdot \mu$ and $v_R = \pm v \sqrt{1 - \mu^2}$, where $v = \sqrt{2\varepsilon/m}$, m being the mass of the electron. It is noted that the velocity space is spherically symmetric around the x axis (i.e. all radial directions are equivalent). The sign of v_x indicates the direction of the electron's velocity: the dots on the half plane $v_x > 0$ correspond to electrons moving from the CDS to the NG and on the half plane $v_x < 0$ to those moving from the NG towards the CDS. In Figs. 6 and 7 the angular distri-

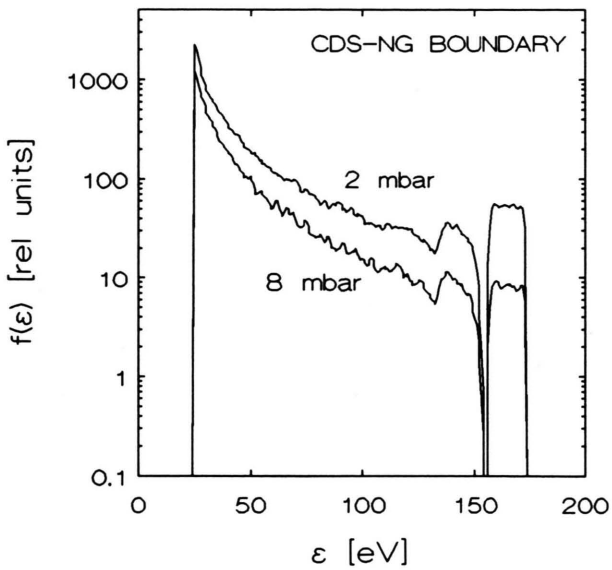

Fig. 3. The EEDF at the CDS-NG boundary ($x = d$) of the hollow cathode discharge at 2 and 8 mbar pressures.

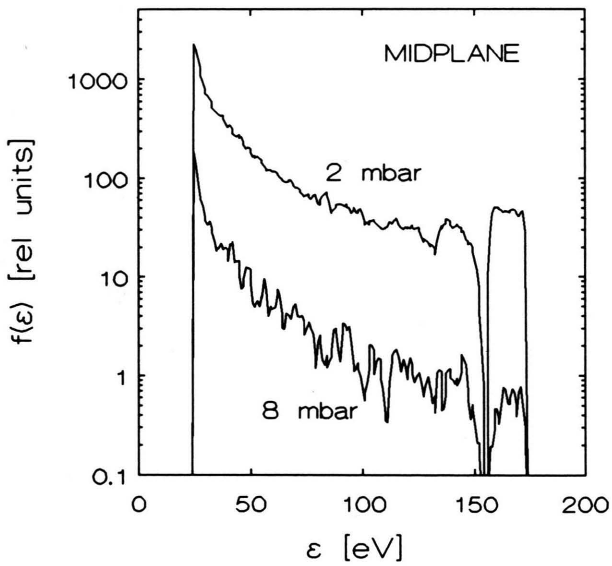

Fig. 4. The EEDF at the midplane of the hollow cathode discharge ($x = L/2$) at 2 and 8 mbar pressure. (The increased noise of the EEDF at 8 mbar occurs because of the small number of electrons reaching the midplane of the discharge at this pressure.)

bution is plotted at the CDS-NG boundary ($x = d$) at pressures of 2 and 8 mbar. It can be seen in Figs. 6 and 7 that the electrons enter the NG in a quite wide range of angles. The dots on the $v_x < 0$ half plane in Fig. 6 indicate that at 2 mbar there is a significant

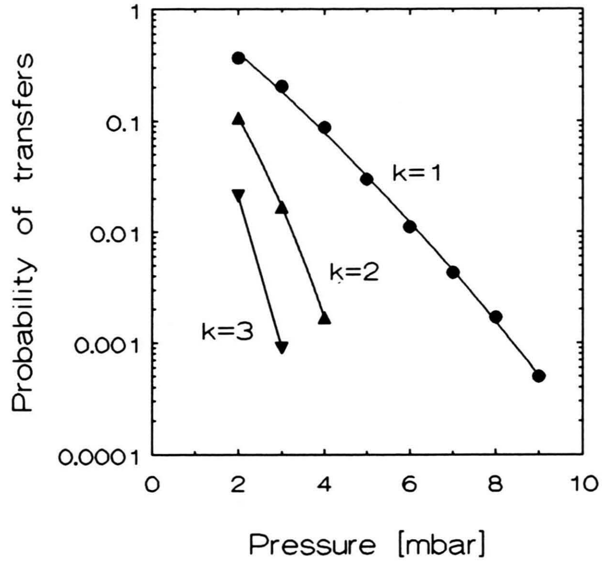

Fig. 5. The probability of $k = 1$, 2 and 3 transfers of primary electrons through the negative glow as a function of gas pressure.

backward flux of electrons into the CDS from the NG. This flux consist of electrons which are backscattered from the NG, created in the NG in an ionization process or came through the NG from the opposite CDS. At 8 mbar the number of electrons that cross the NG is marginal (see Figure 5). The result of this can be clearly seen in the phase plane plot of Fig. 7: the number of backward moving high energy electrons is very small.

In the HC discharge the electrons starting from both cathodes contribute to the ionization in the negative glow and even in the "opposite" cathode dark space. Figure 8 shows the source function $\partial n^+(x)/\partial t$ of He^+ ions at $p = 4$ mbar pressure. The total source function is the sum of two functions corresponding to the electrons (and electron avalanches) starting from the "left" and "right" cathodes. The total source function exhibits a characteristic behaviour as the operating pressure is changed. This dependence is plotted in Figure 9.

The current balance at the cathode is defined as the ratio of the ion to the electron current density j^+/j^-. In plane cathode discharges in helium den Hartog et al. have found a typical value ≈ 3.3 for the current balance [24]. It was noted by them that this value does not imply a secondary emission coefficient of ≈ 0.3 for ion impact since other electron emission processes

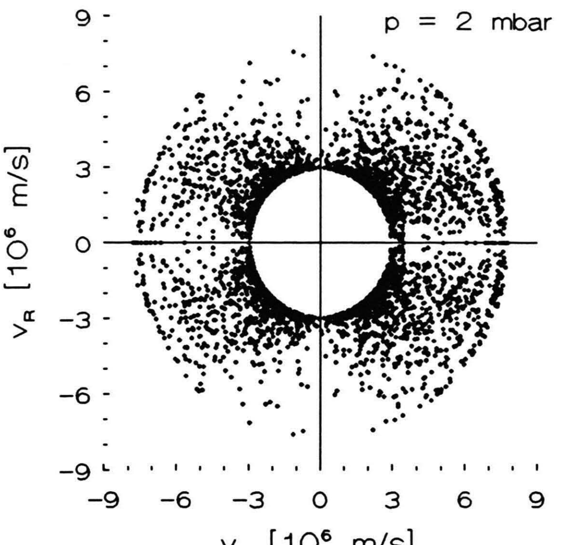

Fig. 6. Distribution of the velocity of high-energy electrons crossing the CDS-NG boundary ($x = d$) plotted on the (v_x, v_R) phase plane at $p = 2$ mbar.

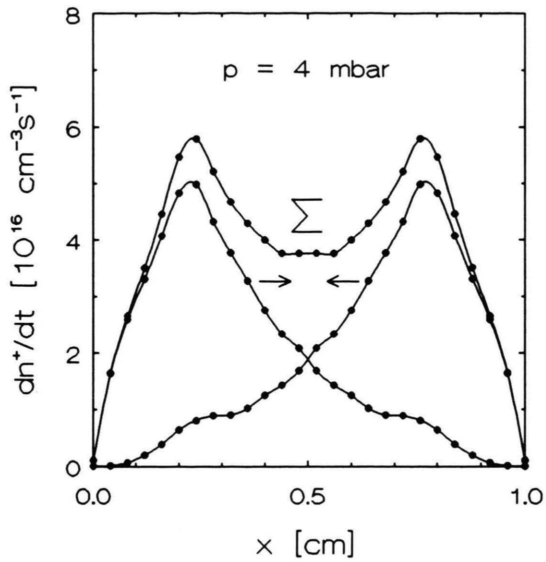

Fig. 8. The spatial distribution of the source function of He^+ ions at $p = 4$ mbar pressure. The arrows (→ and ←) indicate the source functions corresponding to electron avalanches started from the "left" and "right" cathodes, respectively. Σ indicates the total source function.

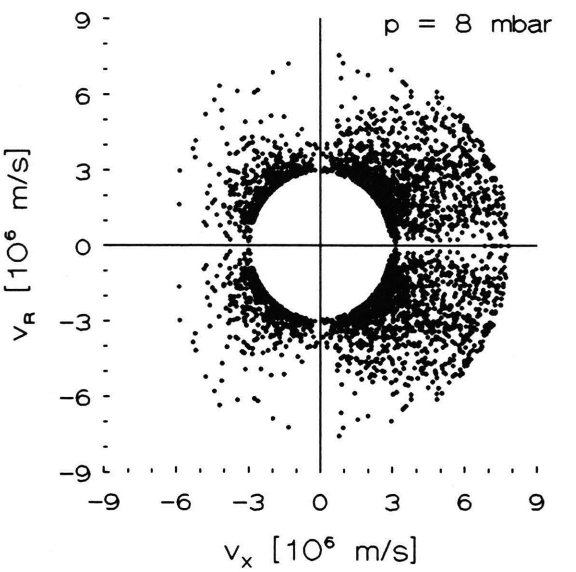

Fig. 7. Distribution of the velocity of high-energy electrons crossing the CDS-NG boundary ($x = d$) plotted on the (v_x, v_R) phase plane at $p = 8$ mbar.

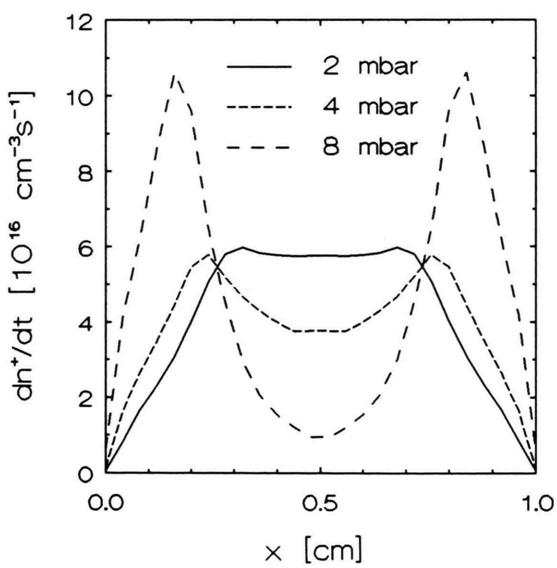

Fig. 9. The spatial distribution of the total source function of He^+ ions at $p = 2$, 4 and 8 mbar pressure.

than ion impact may also take part in the maintenance of the discharge. The results for the current balance of the present Monte Carlo simulations are shown in Figure 10. At higher pressures, where the discharge behaves more like a plane single cathode discharge, the obtained current balance values are close to 3. With decreasing pressure (i.e. towards the hollow cathode operation mode) j^+/j^- decreases significantly. This indicates even without the knowledge of the actual electron emission coefficients of the dif-

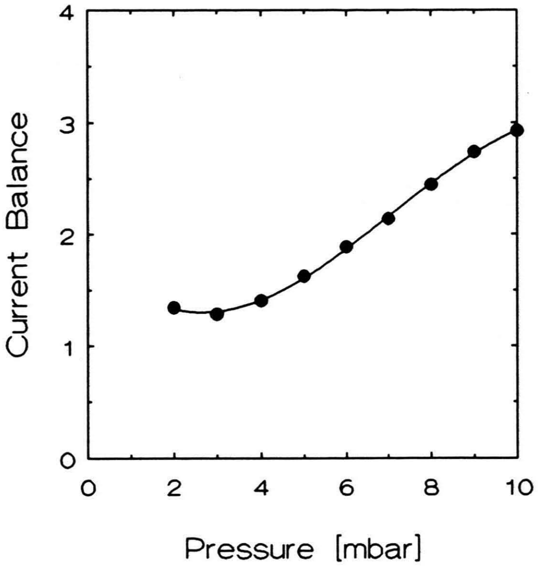

Fig. 10. The dependence of the current balance j^+/j^- at the cathode of the discharge on helium pressure.

ferent processes that other processes than ion impact become more important at lower pressures. This is in accordance with the observation that in hollow cathode discharges the enhanced UV radiation from the NG contributes in a significant way to the maintenance of the discharge.

5. Conclusions

The motion of high energy ($\varepsilon > E_i = 24.56$ eV) electrons in a helium hollow cathode discharge has been studied using Monte Carlo simulation. The length of the CDS in the plane parallel HC discharge was determined by applying the simulation in an iterative way and using experimentally measured current density-voltage characteristics. The calculations were carried out in the pressure range of 2–10 mbar at $j = 1$ mA/cm^2. The low value of the current density justifies the ignorance of cumulative processes and thermal effects.

The comparison of the electron energy distribution functions (EEDF) at the CDS-NG boundary and at the midplane of the discharge showed that there is a strong pressure dependence: The concentration of high energy electrons

- is about the same at the two positions at 2 mbar,
- at 8 mbar pressure it is by 1 and 2 orders of magnitude smaller than at 2 mbar at the CDS-NG boundary and at the midplane, respectively.

As it was expected at low pressures many electrons cross the negative glow. At 2 mbar the probability of 1, 2 and 3 transfers for primary electron were found to be 37%, 11% and 2%, respectively. The decrease of the transfer probabilities with increasing pressure is close to exponential. These results support the possibility of multiple transfers of electrons through the negative glow, i.e. the existence of oscillating electrons.

The angular distribution of the electron velocity at the CDS-NG boundary was found to be rather wide. The phase plane portraits at the CDS-NG boundary indicated the backscattering of electrons from the NG, and also that at low pressures there exists a significant flux of high energy electrons from the "opposite" CDS.

The source function corresponding to electron impact ionization showed a characteristic pressure dependence.

The pressure dependence of the current balance (j^+/j^-) at the cathode indicated that with decreasing pressure other secondary electron emission processes than ion impact become more important.

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[1] P. F. Little and A. von Engel, Proc. Roy. Soc. London **A 224,** 209 (1954).
[2] A. von Engel, Ionized Gases, Clarendon Press, Oxford 1965.
[3] Y. M. Kagan, J. Phys. D: Appl. Phys. **18,** 1113 (1985).
[4] S. Hashiguchi and M. Hasikuni, Japanese J. Appl. Phys. **26,** 271 (1987).
[5] S. Hashiguchi and M. Hasikuni, Japanese J. Appl. Phys. **27,** 1010 (1988).
[6] S. Hashiguchi and M. Hasikuni, Japanese J. Appl. Phys. **27,** 2007 (1988).
[7] S. Hashiguchi, IEEE Transactions on Plasma Science **19,** 297 (1991).
[8] A. Walsh, Spectrochimica Acta **7,** 108 (1955).
[9] P. Apai and K. Rózsa, in: Proceedings of Pentagonale Workshop on Elementary Processes in Clusters, Lasers, and Plasmas (T. D. Märk and R. W. Schrittwieser, eds.), Kühtai, Austria 1991, p. 286.
[10] R. Solanki, E. L. Latush, D. C. Gerstenberger, W. M. Fairbank, Jr., and G. J. Collins, Appl. Phys. Lett. **35,** 317 (1979).
[11] K. Rózsa and M. Jánossy, in: Proceedings of the XVIth International Conference on Phenomena in Ionized Gases, Düsseldorf, invited papers (W. Bötticher, H. Wenk, and E. Schulz-Gulde, eds.), 150 (1983).
[12] M. Jánossy, P. Mezei, P. Horváth, and L. Csillag, Opt. Commun. **68,** 58 (1988).
[13] P. Mezei, P. Apai, M. Jánossy, and K. Rózsa, Opt. Commun. **78,** 259 (1991).
[14] H. Helm, Z. Naturforsch. **27a,** 1812 (1972).
[15] A. Güntherschulze, Z. Physik **19,** 313 (1923).
[16] H. Helm, H. F. Howorka, and M. Pahl, Z. Naturforsch. **27a,** 1417 (1972).
[17] R. Kollath, Encylopedia of Physics, Vol. XXI, Springer, Berlin 1956, p. 263.
[18] H. Helm, Beitr. Plasmaphysik **18,** 233 (1979).
[19] T. Iijima, T. Arai, K. Nihira, and T. Goto, in: Proceedings of the XVIIIth International Conference on Phenomena in Ionized Gases, Swansea, contributed papers (W. T. Williams, ed.), Vol. 1, 66 (1987).
[20] R. M. Chaudhri, M. M. Chaudhri, F. Deba, and M. N. Chaudhri, Int. J. Electronics **62,** 679 (1987).
[21] Tran Ngoc An, E. Marode, and P. C. Johnson, J. Phys. D: Appl. Phys. **10,** 2317 (1977).
[22] J. P. Boeuf and E. Marode, J. Phys. D: Appl. Phys. **15,** 2169 (1982).
[23] M. Ohuchi and T. Kubota, J. Phys. D: Appl. Phys. **16,** 1705 (1983).
[24] E. A. Den Hartog, D. A. Doughty, and J. E. Lawler, Phys. Rev. A **38,** 2471 (1988).
[25] R. J. Carman, J. Phys. D: Appl. Phys. **22,** 55 (1989).
[26] M. Yumoto, Y. Kuroda, and Y. Sakai, J. Phys. D: Appl. Phys. **24,** 1594 (1991).
[27] A. Date, K. Kitamori, Y. Sakai, and H. Tagashira, J. Phys. D: Appl. Phys. **25,** 442 (1992).
[28] M. Dalvie, S. Hamaguchi, and R. T. Farouki, Phys. Rev. A **46,** 1066 (1992).
[29] Z. Donkó and M. Jánossy, J. Phys. D: Appl. Phys. **25,** 1323 (1992).
[30] D. A. Doughty, E. A. Den Hartog, and J. E. Lawler, Phys. Rev. Lett. **58,** 2668 (1987).
[31] H. R. Skullerud, J. Phys. D: Appl. Phys. **1,** 1567 (1968).
[32] F. J. de Heer and R. H. J. Jansen, J. Phys. B: At. Mol. Phys. **10,** 3741 (1977).
[33] J. C. Nickel, K. Imre, D. F. Register, and S. Trajmar, J. Phys. B: At. Mol. Phys. **18,** 125 (1985).
[34] H. D. Hagstrum, Phys. Rev. **104,** 317 (1956).
[35] O. B. Firsov, Zh. Eksp. Teor. Fiz. **21,** 1001 (1951).
[36] S. Shinha and J. N. Bardsley, Phys. Rev. A **14,** 104 (1976).
[37] D. Rapp and W. E. Francis, J. Chem. Phys. **37,** 2631 (1962).