Measurements of EEDF in recombination dominated afterglow plasma

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Abstract. Electron energy distribution functions (EEDF) have been measured in decaying plasma in Flowing Afterglow Langmuir Probe (FALP) experiment. The measurements have been carried out in diffusion and recombination governed plasmas used for studies of recombination of KrD⁺ and H₃⁺ ions.

1. Introduction
Recombination of ions with electrons and diffusion are two important processes controlling degree of ionisation in low temperature plasmas. Typical low temperature plasma is the afterglow plasma, which is formed in an active discharge, and decays after termination of ionisation or after moving out from the region with ionisation. If gas is flowing through a discharge region, e.g. along a tube, it can take plasma away from the discharge and the plasma will then decay along the flow of gas. Such “Flowing Afterglow” (FA) is used to study relaxation processes, ion-molecule reactions and electron–ion recombination. In principle decaying plasma in FA is not in thermodynamic equilibrium, nevertheless it can be very close to thermodynamic equilibrium. Validity of the assumption of equilibrium has to be discussed for particular experimental conditions and verified by measuring plasma parameters. Further we will discuss FALP experiment (Flowing Afterglow with Langmuir Probe) and experimental conditions used for recombination studies when helium is used as a buffer/carrier gas. In FALP experiments it is usually assumed that afterglow plasma is thermalised, \( T = T_e = T_{\text{ion}} = T_{\text{He}} \). We will show that such assumption is not always fulfilled. The clear misbalancing factor in helium afterglow is a presence of internally excited long-lived particles formed in He discharge, in ion-molecule reactions, and in recombination. In the majority of FALP experiments Ar is added to helium flow immediately downstream from the discharge region to quench helium metastables (He(2⁢S) and He(2¹S)) formed in the discharge. After addition of Ar these metastables are removed from the plasma by Penning ionisation and plasma relaxes rapidly, this process is clear and well described [1].

We will study processes connected with recombination and with formation of recombination dominated plasma (demonstrated on Ar⁺, Kr⁺, KrD⁺ and H₃⁺). In these processes energetic electrons and heavy excited particles can be formed. In Penning ionisation and in superelastic collisions these excited particles can transfer their internal energy to electrons of already cold decaying plasma. The generation of energetic electrons can influence the electron energy distribution function (EEDF) [2].
and the decay of the plasma. Further plasma decay depends on the balance between generation, recombination, thermalisation and diffusion of electrons.

2. Experiment

The principle of the FALP method used in the present experiments is shown in Fig. 1. Helium buffer gas flows (at pressure $p_{\text{He}} = 1600$ Pa) through the glass discharge tube and He$_2^+$ dominated plasma is generated by microwave excitation. The flowing buffer gas then drives plasma along the flow tube, where reactant gases required for the formation of studied ions can be introduced via injection ports (P1 and P2 are 3 and 35 ms downstream from the discharge, respectively).

![Figure 1. Principle of FALP method.](image)

The plasma parameters (including EEDF) are determined by measuring probe characteristics ($I_{\text{Probe}}$ versus $U_{\text{Probe}}$) with axially movable Langmuir probe. Example of electron energy probability function (EEPF) obtained in Ar$^+$ dominated late afterglow plasma (at $t = 45$ ms) in He/Ar mixture is plotted in Fig. 2. The plasma is not recombining and decays only due to diffusion losses. Plotted is “uncorrected” EEPF calculated from the second derivative of probe current ($I_{\text{Probe}}''$) using Druyvesteyn formula and “corrected” EEPF [3, 4]. The EEPF ($f_{\text{EEPF}}$) is connected with corresponding EEDF ($f_{\text{EEDF}}$) by the formula $f_{\text{EEDF}}(\epsilon) = f_{\text{EEPF}}(\epsilon) \cdot \sqrt{\epsilon}$. Advantage of EEPF is that for Maxwellian EEDF the corresponding EEPF is exponential, i.e. in semilogarithmic plot it is a straight line. The measured EEPF is nearly Maxwellian over the whole covered range of electron energies. The obtained electron temperature is $T_e = 360$ K i.e. it is slightly higher than $T_{\text{He}}$, $\Delta T_e \sim +110$ K. The increase can be caused by presence of excited Ar$^+$ ions in $^1P_{1/2}$ spin state, with excitation energy $\Delta \epsilon = 0.18$ eV. These ions formed in Penning ionisation can transfer energy to electrons in superelastic collisions.

![Figure 2. Electron energy probability function (EEPF) obtained from measured characteristic of Langmuir probe.](image)

Part of the increase of $T_e$ is probably also due to systematic error of the measurements due to the fluctuation of plasma potential, potential of the probe and inhomogeneity of the probe surface. We suppose that the systematic increase given by “apparatus effect” of the technique used is $\delta T_e \sim +70$ K. The evolution of EEPF (normalised to electron density) in Ar$^+$ dominated afterglow is shown in Fig. 3. In the inset evolutions of electron density ($n_e$) and electron temperature ($T_e$) are plotted. The exponential decay of $n_e$ corresponds to diffusion losses. Note that $T_e$ is higher at low decay time and it is decreasing towards higher decay time, from 450 K to 350 K, this corresponds $T_e = 380-280$ K after subtraction of $\delta T_e \sim +70$ K.
but the electron temperature is higher than in Ar$^+$ dominated plasma. The measured $T_e$ decreases during afterglow from 600 K to 450 K. From this $\delta T_e \sim +70$ K can be attributed to the already discussed “apparatus effect”, but higher increase is due to transfer of energy from the metastable particles. We suppose, that the increase is connected with presence of Kr$^+$($^2\text{P}_j$,2), which can in superelastic collision transfer excitation energy ($\Delta \varepsilon = 0.67$ eV) to electrons, and in consequent electron – electron collisions the energy is transferred to electron gas. Because the plasma is not recombining we do not see other source of energy, which can heat electrons along the flow tube. The electron density gradients and gradients of electric potential are comparable with Ar$^+$ dominated plasma. At the position of port P2 and further downstream Maxwellian EEDF was observed.

### 3. Measurements of EEDF in recombining plasma

If krypton is added instead of Ar to the helium via P1, then in following ion molecule reactions and Penning ionisation Kr$^+$ dominated plasma is formed. Kr$^+$ ions in two spin states, $^2\text{P}_{3/2}$ (ground state) and $^2\text{P}_{1/2}$ are present in such plasma. At the position of port P2 and further downstream Maxwellian EEDF was observed.

The situation is different if deuterium is introduced via the port P2 to the above-described Kr$^+$ dominated afterglow plasma (with Maxwellian EEDF). The used density of D$^+$ is low in comparison with Kr density, $[\text{D}_2]/[\text{Kr}] \sim 0.1$. In the sequence of ion-molecule reactions ions KrD$^+$ and D$^+$ are formed. The densities of these two types of ions are in equilibrium and the ratio $[\text{KrD}^+]/[\text{D}_2]$ = $K_{\text{eq}}[\text{Kr}]/[\text{D}_2]$, where $K_{\text{eq}}(T_{\text{he}})$ is corresponding equilibrium constant. Because of the low value of $[\text{D}_2]/[\text{Kr}]$ the KrD$^+$ ions are dominant in the decaying plasma. The formation of KrD$^+$ from Kr$^+$($^2\text{P}_j$,2) is exergic by $\sim 1.2$ eV, from Kr$^+$($^2\text{P}_j$,2) by $\sim 1.9$ eV. The excess energy gained from exothermicity of reactions can be stored in internal excitation of KrD$^+$ and in superelastic collisions transferred to electrons. The measured EEPFs (normalised to electron density) are plotted in Figure 4. The production of energetic electrons is evident. The variation of the high-energy part of EEPF along the flow tube is coupled with decrease of electron density and “cut off mechanism” [5]. The high-energy group of electrons does not exceed 2% of all electrons. The body of EEPF is Maxwellian and can be characterised by the temperature. The high-energy group does not directly influence the measurements of recombination rate coefficient ($\alpha \sim 2 \times 10^{-8}$ cm$^3$s$^{-1}$); nevertheless it influences the electron temperature of the recombining plasma. The measured experimental data have been compared with EEDF obtained by numerical calculations assuming source of energetic electrons (assuming $e_{\text{eqn}} = 0.7$ eV). The numerical simulation describes
the temporal evolution of the EEDF in the presence of electron – electron (Coulomb) collisions and electron – helium atom collisions. Monte Carlo approach is used for electron – neutral collision modelling. The preliminary results are in agreement with measured EEDF, further calculations are in progress to improve the model.

If hydrogen is added via port P2 to Ar$^+$ dominated plasma described in experimental section (see also Fig. 3), H$_3^+$ dominated plasma is formed within few centimetres from the port. In this plasma recombination is fast loss process ($\alpha \sim 2 \times 10^{-7}$ cm$^3$ s$^{-1}$, see accompanying paper in present volume). The measured evolution of EEPF together with the calculated ionic composition and measured decay of electron density are plotted in Fig. 5. In the first 10 ms the EEPF exhibits a high energy group, during the further decay the deviation disappears and electrons are nearly thermal; nevertheless the temperature is slightly higher than in Ar$^+$ dominated plasma. This observation is in qualitative agreement with our recent model of multicollisional character of H$_3^+$ recombination. Further studies are in progress.

4. Conclusion
We measured EEDF and its evolution during diffusion and recombination governed afterglow in FALP. The experimental conditions were identical with those in the case of recombination studies of H$_3^+$ and KrD$^+$. The low-energy part of EEDF is close to Maxwellian and the corresponding temperature can be used to characterise electron gas in the decaying plasma. The heating due to inelastic processes, causing increase of electron temperature, is observed. Only very small fraction of electrons is not Maxwellian (<2%), so the measured rate coefficient can be considered as thermal, corresponding to temperature of the body of the EEDF. The calculation of EEDF under assumption of production of fast electrons supports measured data.

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References
[1] Glosík J, Báňo G, Plašil R, Luca A and Zakouril P 1999 *Int. J. Mass Spectrom.*, 189 103–113
[2] Kolokolov N B, Kudrjavtsev A A and Blagoev A B 1994 *Physica Scripta* 50 371–402
[3] Gorbunov N A, Grochola A, Kruk P, Pietruczuk A and Stacewicz T 2002 *Plasma Source Sci. Technol.* 11 492–497
[4] Korolov I, Plašil R, Kotrík T, Dohnal P, Novotný O and Glosík J 2008 *Contrib. Plasma Phys.* 48 461-466
[5] Arslanbekov R R, Kudryavtsev A A and Tsendin L D 2001 *Phys. Review E* 64 016401