Model for describing non-equilibrium helium plasma energy level population

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Abstract. A new method for calculating the population of excited levels of helium atoms and ions is suggested. The method is based on direct solution of a system of balance equations for all energy levels for which it was possible to obtain process speed constants. The equations include terms for the processes of particle loss and income by excitation and deexcitation, ionization and recombination as well as losses due to diffusion and radiation. The challenge of solution of such large system is also discussed.

1. Introduction
The aim of the work is development of methods for determination of plasma composition and its basic parameters from its radiation properties when strong deviations from equilibrium are taking place thus limiting the applicability of a number of existing diagnostics approaches. One of the requirements to the developed methods is minimization of input parameters (down to plasma pressure, plasma-forming gas component quantities and power consumed by plasma arc). This will allow using the developed methods for processing experimental data as well as for selecting optimal experimental parameters. In this work, experiments on helium plasma generation at atmospheric pressure were carried out and its emission spectra were recorded with the AvaSpec three-channel spectrometer and DFS-452 monochannel spectrometer. The former allows registering plasma emission spectra in a wide wavelength range from 200 to 1100 nm while the latter registers in a comparably moderate wavelength range but has a very narrow apparatus function (about 0.02 nm).

2. Processing of experimental data
The spectra were processed with the developed automatic processing software. It performs the following steps:

- spectral line peak positions are determined from the experimental spectrum points;
- for each peak position, an interval containing spectrum points belonging to the line is determined;
- the found experimental line is matched to a known line in a NIST spectral line table [1].

This allows determining such line parameters as transition energy and statistical weights;
the line contours of each line are approximated by a Voight function using a best-fit algorithm. Line width and other parameters are determined from the fitted function parameters;

- radiation intensity of each line is found as an integral over the contour of Voight function;
- continuum radiation intensity at the wavelengths close to a found line is assumed to be equal to the value of Voight fitted function for this line far from its center.

Figure 1 shows a distribution of relative excited level populations in Helium plasma at arc current of 200 A in 6 mm from cathode. The corresponding line wavelengths are given for every point. The obtained distributions do not agree with the Boltzmann law with single electron temperature, showing that the plasma ion composition deviates significantly from the equilibrium state in the axis region. The Boltzmann exponent method, when applied to the obtained data (a typical set of points is shown in figure 1), has given the electron temperature value of 7000–10000 K, what is about three times lower than the heavy particle temperature found from the Doppler widening. This disagreement confirms the existence of deviations from equilibrium in plasma composition. Therefore, a special method is needed to determine electron temperature from atom distributions over the excited states.

### 3. Modeling of excited state population in non-equilibrium state

The fact that helium plasma at atmospheric pressure at temperatures from 1 to 5 eV is in non-equilibrium state has been noted by various authors. In [2] it is stated that high energy levels ($n > 5$) tend to equilibrium with continuum while lower energy levels are overpopulated. This statement has been experimentally proven in [3]. In case of helium deviation from equilibrium state is substantiational even under conditions when, for example, argon plasma does not strongly show them [4–6]. The authors of these works suggest their own approaches for analysis of such systems based on simple analytical estimations. However this approach is too approximate for quantitative analysis of experimental spectroscopic data. In [2] the following methods are suggested for describing these non-equilibrium distributions: modified diffusion approach and solution of system of kinetic equations for balance of excited level population. The necessity to use special methods for helium plasma is also noted in [7] where a more elaborate collisional-ionizational model is described allowing to make a more detailed description of excited level structure and of transitions between them. Such approaches had been suggested in earlier works as well [8], but on a lower qualitative level because complex calculations of speeds of a multitude of processes were an impossible task for computers at that time. However, now this approach appears to be rather feasible. The applicability of collisional-ionizational model for
description of helium plasma is solidly proven in [7]. The authors have collected a large set of contemporary achievements on this theme and have suggested a model allowing to determine electron temperature $T_e$ and concentration $n_e$ for the case of low ionization of stationary plasma. The data and approaches used in this work can be partially used to solve a more complex and ambitious task—construction of a non-stationary helium plasma model applicable even for cases when ion concentration is considerable. Based on the foregoing, in order to solve the task to analyze the structure of helium plasma excited level population a system of equations will be solved without using approximate solutions [2, 8], using a possible minimum of approximations used in [7] and using experimental data on cross-sections and process speeds where possible. We abandoned a simplified system of energy levels—the system of equations includes all energy levels found in NIST database. The excited states of helium atoms are considered together with excited states of first level ions and second level ion base state. The main feature of our calculation scheme is that the solution of Saha equations to determine concentrations of charged particles, which is inapplicable in our case, is not used. Instead, they are found through the solution of equations of process kinetics in which they are used as unknown variables.

As stated before, the values of electron and heavy particle temperatures found with Boltzmann exponent and Doppler widening methods disagree significantly. The reasons for the deviation of atomic distribution on the excited levels may include the following:

(i) actual difference between electron and heavy particle temperature;

(ii) high values of transfer coefficients in helium, what leads to the loss of charged particles from the arc and domination of ionization process over the recombination process in the arc;

(iii) high gap between the energies of base and first excitation state of helium (19.82 eV).

In our case, the first factor does not have any influence because the plasma is isothermal.

The phenomenon described in the second item takes place in our case because the arc in question had the diameter of only 3 mm, therefore the influence of charged particle loss due to diffusion on the plasma composition is significant. The times of equilibrium setup in atomic and ion subsystems of plasma are of micro- and millisecond order respectively while the speed of charged particle loss due to diffusion is about $2 \times 10^{-5}$ s. Therefore, the ionized particle creation speed can be assumed to be comparable to the speed of charged particle loss.

The third effect also has its part in the deviation. For gases with lower values of transfer coefficients, the described deviations do not occur in similar to our experimental conditions. In case of helium the block of excited states is located in almost 20 eV from the base state, the ionization energy of helium is 24.58 eV and the distance between levels $n > 5$ is of 0.1 eV and 0.01 eV order. Because of this, the probabilities to excite any high-energy state at the electron temperatures of about 2 eV are almost equal. Furthermore, at temperatures, which are enough for noticeable concentrations of excited particles to appear, electron collisions cause cascade excitations over the close-lying excited levels with consequent ionization causing quick depopulation of excited levels. As a result, the following is observed: the population speeds of excited states do not appear to be varying much for states at different distance from ionization energy, however, the depopulation speeds increase sharply for levels close to ionization energy. This also leads to the distortion of excited particle distribution.

In [2] it is noted that the higher-energy excited states ($n > 5$) tend to equilibrium with continuum while lower-energy excited states are overpopulated. This statement has been experimentally confirmed in many works including the current one. For the case of helium, the deviation from the equilibrium state is substantial even under conditions, when, for example, argon plasma does not show these phenomena. The author suggests the so-called modified diffusion approach as a method for describing such nonequilibrium distributions where the combination of discrete energy levels is replaced with a certain continuous distribution what can be justified for high-energy states. However, the applicability of this approach for lower...
energy states is questionable, especially for the case of helium where the energy gaps between lower energy levels are large.

Based on the foregoing, in order to solve the task to analyze the structure of helium plasma excited level population a system of equations will be solved without using approximate solutions [2, 8], using a possible minimum of approximations used in [7] and using experimental data on cross-sections and process speeds where possible. We abandoned a simplified system of energy levels the system of equations includes all energy levels found in NIST database. The excited states of helium atoms are considered together with excited states of first level ions and second level ion base state. The main feature of our calculation scheme is that the solution of Saha equations to determine concentrations of charged particles, which is inapplicable in our case, is not used. Instead, they are found through the solution of equations of process kinetics in which they are used as unknown variables.

The following assumptions were made for this task:

(i) there equilibrium distribution of atoms over the excited states is not present (Boltzmann distributon and Saha equations do not describe the distribution correctly);
(ii) the plasma is optically thin (the radiated energy cannot be absorbed elsewhere in plasma body);
(iii) the working gas contains no admixtures.

The system of equations as follows:

$$\frac{dHeI_k}{dt} = \sum_{m=1}^{N} [HeI_m \cdot n_e \cdot kI_{Emk} - HeI_k \cdot n_e \cdot kI_{Qkm}] +$$

$$\sum_{m=1}^{M} [HeII_m \cdot n_e \cdot kI_{Rmk} - HeI_k \cdot n_e \cdot kI_{Qkm}] - Rad_k - D_{HeI},$$

$$\frac{dHeII_i}{dt} = \sum_{m=1}^{N} [HeI_m \cdot n_e \cdot kI_{Imi} - HeII_i \cdot n_e \cdot kII_{Rmi}] +$$

$$+ \sum_{m=1}^{M} [HeII_m \cdot n_e \cdot kII_{Emi} - HeII_i \cdot n_e \cdot kII_{Qmi}] +$$

$$(n_e^2 \cdot HeIII \cdot kII_{R3} - n_e \cdot HeII_i \cdot kII_{Ri}) - Rad_k - D_{HeII},$$

$$\frac{dHeIII}{dt} = \sum_{m=1}^{M} (n_e \cdot HeIIIm \cdot kII_{Im} - n_e^2 \cdot HeIII \cdot kII_{Rm}) - D_{HeIII}. $$

Next are the variables seen in this system. \( N \) and \( M \) are the number of excited states of helium atom and first level ion respectively; \( He... \) are the excited particle concentrations at different excitation levels:

- \( HeI_k \)—concentration of HeI (atom) at \( k \)-th excited level;
- \( HeII_k \)—concentration of HeII (first level ion) at \( k \)-th excited level;
- \( HeIII \)—concentration of HeIII (second level ion);
- \( n_e \)—electron concentration; \( k \) denotes transition process speed values:
  - \( kI_{Emk} \)—HeI excitation from \( m \)-th to \( k \)-th level by an electron impact;
  - \( kI_{Qkm} \)—HeI deexcitation from \( k \)-th to \( m \)-th level by electron impact;
  - \( kI_{Rmk} \)—HeII three-particle recombination from \( m \)-th level to HeI \( k \)-th level;
• \(k_{IIkm}\) — HeI impact ionization from \(k\)-th level to HeII \(m\)-th level;
• \(k_{IIEmi}\) — HeII excitation from \(m\)-th to \(i\)-th level by an electron impact;
• \(k_{IIQim}\) — HeII deexcitaiton from \(i\)-th to \(m\)-th level by electron impact;
• \(k_{IIRmi}\) — HeII three-particle recombination from \(m\)-th level to HeI \(i\)-th level;
• \(k_{IIIi}\) — HeII impact ionization from \(k\)-th level to HeIII;
• \(k_{IIIi}\) — HeII three-particle recombination from \(m\)-th level to HeII \(i\)-th level;

\(Rad_k\) and \(D\) are concentration losses due to radiation and diffusion respectively.

The system of equations is augmented by Mendeleev-Klapeyron equation to make the number of equations ans unknowns equal. The derivatives on the left-hand side are equal to zero because the considered task is stationary and are shown only to give indices of the corresponding particles in the equation.

The required constants for all considered states—excitation energies, statistical weights, oscillator strengths—have been obtained from the NIST Atomic Spectra Database [1]. The excitation levels used in the calculation are the levels for which the NIST database provides all necessary constants. The rest of the levels are low-populated and neglecting them does not introduce considerable errors into the calculation results. The transition process speeds for all energy levels at the given temperature are calculated beforehand and substituted into the system of equations as constants. Thus, the system of equations contains only concentrations of particles at all possible energy levels as unknowns in first, second or third power and the challenge is to find roots of the system of 113 non-linear equations (derived from the number of considered excited states and auxiliary equations).

4. First results and found problems

The tests run on a system of 17 equations including only a part of excited levels have shown that the system of equations is extremely stiff and it is impossible to obtain a correct solution on a PC using double (64-bit) precision used in most mathematical software. The values on which an iterative procedure converges are affected by round-off errors to such extent that substituting the obtained answer values back into the equations yields equation inagreement of a magnitude comparable to that of the found values themselves.

The available mathematical software, which is capable of performing variable-precision arithmetics, is Waterloo Maple, Wolfram Mathematica and Mathworks MATLAB (the latter has limited support). To solve the system, Maple was selected for being a reasonable trade-off between calculation capabilities and easiness of application.

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