Spectral measurements of electron temperature in nonequilibrium highly ionized He plasma

O V Korshunov1, V F Chinnov1, D I Kavyrshin1 and A G Ageev2

1 Joint Institute for High Temperatures of the Russian Academy of Sciences, Izhorskaya 13
Bldg 2, Moscow 125412, Russia
2 National Research University Moscow Power Engineering Institute, Krasnokazarmennaya 14,
Moscow 111250, Russia
E-mail: ageevalex@yandex.ru

Abstract. It has been experimentally shown that highly ionized He arc plasma does not achieve local thermodynamic equilibrium expected for plasmas with electron concentrations above $1 \times 10^{16}$ cm$^{-3}$ like argon plasma. We have found that the reason for this deviation is strong nonisotropy of plasma. Triple electron recombination with temperatures of 2.5–3 eV is almost absent. Charged particles move from the arc ($r = 1$ mm) to chamber walls due to ambipolar diffusion creating ionization nonequilibrium over the excited states rendering Boltzmann distribution and Saha equation inapplicable for determining electron temperature. A method for determining electron temperature is suggested that is based on using the relative intensities of the atomic and ion lines. Its advantage lies in an energy gap between these lines’ states over 50 eV that reduces the influence of nonequilibrium on the result. This influence can be taken into account if the ionization energies of emitting states of atom and ion have close values. The suggested method can be expanded for any media including those with dimensional nonisotropy that have both atomic and ion lines in their emission spectra.

1. Introduction

The fact that stationary atmospheric pressure helium arc plasma exists in nonequilibrium state at high temperatures (1–5 eV) has been repeatedly noted in literature [1–7]. The classic monograph [1] states that high-energy excited states tend to equilibrium with the continuum while lower energy states are overpopulated. This is proven experimentally in work [2].

A similar pattern is typical for low-temperature plasma of inert and other gases with an unheated heavy component under the conditions of developed ion-molecular kinetics [1, 8, 9]. Dissociative recombination of molecular ions and electrons causes overpopulation of neutral particle lower excited states being the reason for ionization nonequilibrium of this type of plasmas [9].

The deviation from the equilibrium state for helium plasma takes place even under such conditions when other plasmas, like argon, do not show this behavior [3–5]. The authors of these works propose their own methods of analyzing such systems based on simple analytic estimations, however, this kind of approach is too approximate for quantitative analysis of experimental data.

In [1] the following methods are suggested for describing such nonequilibrium distributions: modified diffusion approach and solution of system of balance equations for the populations of...
excited states. The necessity of using special approaches for helium plasma is also noted in work [6], which justifies and applies a more elaborate collision-radiation model allowing detailed description of the structure of excited states and transitions between them taking into account the whole multitude of energy level kinetics processes. This problem had been solved before [7] but with considerably lower computational capabilities of that time. These approaches are now considered most promising [10].

The kinetic model in [6] utilizes all contemporary proceedings on this topic allowing to determine electron temperature $T_e$ and electron concentration $n_e$ more precisely for the case of lower degrees of ionization in stationary plasma. This model can be used as basis for solving a more complex and major task—designing a model for nonequilibrium helium plasma suitable for a wide range of conditions.

In this article we shall confine ourselves to the subjects of the nature of deviation from equilibrium state for heterogeneous helium plasma and diagnostics features caused by the nonequilibrium. Our task is to develop experimental methods to determine the properties of electrons of such plasma in nonequilibrium state, electron temperature being most important.

2. Experiment

The spectral investigations of plasma were carried out on a direct current electric arc plasmatron with expanding anode channel ($d = 4–8$ mm), arc length 10 mm, vortex arc stabilization [11], helium flow 0.1–0.3 g/s and arc current from 200 to 400 A. This plasmatron generates plasma with temperature up to 2.5 eV and 50% degree of ionization [2]. The hottest part of the arc located near the cathode was investigated. The plasma was heated further with electric impulses with the same polarity as the main arc current, duration 1000–1500 $\mu$s and peak current up to 4000 A. Plasma was heated in this quasistationary manner to temperatures up to 4 eV.

The emission spectra of plasma were registered with an optic fiber three-channel spectrometer AvaSpec and DFS-452 spectrograph with Andor high-speed camera attached to its output. The radial distributions were obtained by applying inverse Abel transforms to the obtained spectra.

The experimental measurements are described in work [2]. The plasma has the following characteristics at current 400 A:

- atom concentration $[\text{He}] = 1.4 \times 10^{17}$ cm$^{-3}$, atom temperature $T_a = 2.1$ eV;
- electron concentration $n_e = [\text{He}^+] = 0.88 \times 10^{17}$ cm$^{-3}$, electron temperature $T_e = 2.8$ eV.

3. Nonequilibrium of highly ionized helium plasma

Experimental data confirm that highly ionized stationary helium arc plasma at atmospheric pressure deviates from the local thermodynamic equilibrium state typical for argon [5, 12], nitrogen [12] and other similar plasmas with electron concentrations over $1 \times 10^{16}$ cm$^{-3}$ [1, 12]. This makes helium plasma a unique subject for spectral investigations with its nonequilibrium state caused by imbalance between ionization and recombination processes.

Figure 1 shows the populations of helium atom excited states near the ionization threshold obtained from the stationary arc with 300 A current. The inclination of the straight averaging line gives the distribution temperature $T_d \approx 0.6$ eV which is 5–6 times lower than the electron temperature and shows the presence of ionization underpopulation of emitting excited levels which increases as level energy approaches ionization threshold.

This accumulating underpopulation causes considerable deviation from the equilibrium between the atoms’ ground state and electron continuum which can be easily estimated from the values of $[\text{He}]$, $n_e$, $T_e$ using the Saha–Boltzmann equations [1]. For the temperature range $T_e = 2.5–3$ eV its value is

$$y_k = y_e^2 = 2 \times 10^{-2} – 3 \times 10^{-3},$$

(1)
where $y_k = n_k / n_k^0$ is the relative population of the high-energy excited states on the border with the electron continuum ($k \to \infty$) to their population in the equilibrium state $n_k^0$. $y_e$ is the same for free electrons [1]. This way we show that the ground state is overpopulated by 50–350 times.

There is no consensus in the reviewed literature on the reasons behind this deviation from the equilibrium state. Among the possible factors causing deformation of atomic distribution over the excited energy levels are considered:

(i) existence of difference between electron and heavy particle temperatures [2];
(ii) high values of transport coefficients in helium which cause loss of charged particles from the arc and consequently the emergence of the ionization nonequilibrium, that is, ionization events happening more frequently than recombination events [4];
(iii) very large gap between the ground and first excited state energies in helium (19.82 eV) [5].

The first factor is untenable because nonequilibrium is observed for the cases of isothermal plasma and at high degrees of ionization when energy level population kinetics is fully determined by electron collisions, that is by the temperature of the electrons [2, 4].

The second factor is most significant for the considered plasma generation conditions. An indirect confirmation of the presence of powerful ambipolar diffusion is the observed radial displacement of radiation intensity maximum of the continuum and spectral lines of HeII ion spectral lines relative to HeI atom spectral lines [13]. This observation proves that the speed of charged particle displacement by arc’s radial electric field is comparable to the ionization speed. This causes deviations from the equilibrium between ionization and recombination processes also causing violation of Saha–Boltzmann distribution of particles.

The third factor also plays a significant role. The energies of excited states of HeII have close values but are almost in 20 eV from the ground state, wherein ionization threshold (24.58 eV) is only 4.7 eV higher than excitation threshold. In order for helium atom excitation take place, high electron temperature is needed at which fast atom ionization and slow atom recombination takes place. This causes ionization nonequilibrium to take place [1].

The described features of helium allow us to understand the reasons for nonequilibrium of its plasma at high electron densities and name the reason behind it.
The reason for helium arc plasma nonequilibrium being observed even in the hottest cathode region with highest ionization speed is its dimensional heterogeneity in the arc’s radial direction. The radius of the light emitting channel near the cathode is smaller than 1 mm. At this scale, the transport properties of helium of which high speed of ambipolar diffusion being the main cause, cause fast transfer of charged particles onto the plasmatron wall (its diameter is less than 5 mm near the cathode). Ionization flow in such heterogeneous plasma is not balanced by the reverse recombination flow and is carried away in outer radial direction. The kinetic system tends to recover the equilibrium being upset by electron overheating in strong electric field.

This proposal on the character of ionization and recombination processes is backed up by experimentally observed radial shift of the ion component radiation maximum relative to atomic component due to insymmetrical location of the arc in the plasmatron channel [13]. The ambipolar diffusion causes ions to move from the center of the channel to the area where the arc is closer to the nozzle wall.

Thus three-body recombination is almost absent in this kind of plasma because the products of helium ionization by electrons are carried out from the plasma faster than they get a chance to take part in three-body recombination with electrons which have high temperature (2.5–3.0 eV). As a result, ionization nonequilibrium of the distributions of atoms and ions over excited states takes place [1], which causes electron temperature measurement difficulties by traditional method of relative populations of emitting levels [12] due to Boltzmann and Saha equations becoming inapplicable to the plasma in this state.

4. Atom and ion excited state population distributions and difficulties in electron temperature determination

Figure 2 shows the dependencies specific for atom and ion population distributions over the excited states for the studied plasma. It is evident that emitting levels are in the areas heavily deviating from Boltzmann equilibrium distributions \( \ln(\frac{n_k}{g_k}) \), and the method of determining \( T_e \) from these distributions slope is not applicable.

There is a small region of lower levels of HeII in equilibrium state as can be seen in figure 2, but these levels cannot be used to determine temperature because the corresponding spectral lines are located in the far ultraviolet region of spectrum and cannot be observed with regular spectrometers. Only three ion lines are located in the commonly observable region of the spectrum.

The region of obtained excited atom population distributions is shown in figure 1. Although it contains a multitude of spectral lines, it occupies a small energy range \( \Delta E_{\text{rad}} \approx 1.5 \) eV and is located close to ionization threshold where ionization nonequilibrium takes place. The electron temperature found from the \( \frac{n_k}{g_k} \) distribution is very small (0.6 eV), proving that methods requiring plasma equilibrium are inapplicable in our case.

In order to describe such nonequilibrium distributions, methods as modified diffusion approximation (MDA) are proposed which simplify the solution of system of kinetic balance equations for the populated states [1]. The MDA model replaces discrete high-energy levels with a continuous distribution which is described by a diffusion approach applicable when the gaps between energy levels are small: \( E_{i1} < T_e \). For the discussed electron temperatures of 2.5–3 eV the application region of MDA covers all excited levels of atoms and ion levels beginning from the third one.

A mathematical consectary of this model is ionization nonequilibrium coefficient called xi-function [1] which gives difference between populations of nonequilibrium stare and equilibrium state described by Boltzmann equation:

\[
\chi(x) = \frac{4}{3\sqrt{\pi}} \int_0^x e^{-t^{1.5}}dt,
\]
Figure 2. Energy level populations for HeI and HeII in nonequilibrium state.

where \( x = I / T_e \), \( I \) is electron-binding level. According to this expression, \( \chi = 1 \) at \( x > 5 \). When \( x < 5 \) and \( \chi(x) < 1 \), the value of \( \chi(x) \) decreases as \( x \) decreases. Since energy level populations are proportional to \( \chi \) under the assumption of three-body recombination negligibility \([1]\), the \( k \)-th energy levels with ionization energy \( I_k < 5T_e \) become increasingly underpopulated as \( I_k \) decreases (see figure 2).

Applying this approach to our data we yield the following (see figure 1): \( I_k = 0.38 - 1.87 \) eV giving small \( x_k \sim 0.1 - 0.7 \) and even smaller \( \chi_k = \chi(x_k) = 10^{-3} - 10^{-1} \) for \( T_e \sim 3 \) eV. This is the region of sharp decrease of population near the ionization threshold. Approximating the experimental points using following formula yields the results shown in figure 1.

\[
y_k = n_k / n_k^0 = \chi_k,
\]

where \( n_k^0 \) is \( k \)-th excitation level population in equilibrium state. Unfortunately, this approach gives close distributions for a wide range of \( T_e \). It can be seen from the picture that the difference becomes substantial (over 60%) only at the end of the distribution and only for large temperature
variation (from 2 to 5 eV). For the usual experimental data point scattering the low sensitivity of the method to temperature variation makes it useful only for crude determination of its possible range.

The reason for the weak dependence of the distribution on $T_e$ is the mutual compensation of the values of $n_k^0(T_e)$ and $\chi_k(T_e)$: as temperature increases, the equilibrium component value also increases while the nonequilibrium component value decreases. This is caused by low range of electron binding energies $\Delta E_{\text{emit}}$, its value being only about half of the electron temperature $T_e \approx 3$ eV. The applicability condition for this method is large value of this range, which is not satisfied in our case: $\Delta E_{\text{emit}} > T_e$.

Nevertheless, the nonequilibrium approximation fits the experimental data much better than the equilibrium approximation (see figure 1). Some disagreement appears only at $T_e < 5$ eV for the levels closest to ionization threshold. Their corresponding spectral lines are weak, are hard to make out in the registered spectra and may give overrated population value due to poor visibility against the continuum spectrum. However, it is more likely that three-body recombination is the cause which increases at energies close to the bounded electron energy level (the values of $y_k$ in (1) and (3) are close for these levels).

Thus, although there is mathematical possibility to take ionization nonequilibrium into account while analyzing excited level populations, neither ion nor atomic line spectra are separately suitable for determining electron temperature reliably.

5. Reliable method for determining electron temperature in highly ionized nonequilibrium plasma

The performed analysis shows that the electron temperature may be determined more precisely by analyzing atomic and ion spectral lines together. The advantage of this approach is that the energy gap between these excited levels is over 50 eV, decreasing the influence of nonequilibrium on the result. Moreover, it can also be taken into account and even eliminated.

Under the conditions of strong ionization nonequilibrium concentrations of excited atoms and ions are bound by this expression [1,9]:

$$n_i^+ n_e = n_j K_{ji}(T_e) \chi_{ij},$$

where

$$K_{ji} = \frac{2g_i}{g_j} \left( \frac{2\pi m T_e}{h^2} \right) \exp \left( -\frac{E_{ji}}{T_e} \right)$$  \hspace{1cm} (5)

is the ionization equilibrium constant between atomic and ion excitation level,

$$\chi_{ij} = \chi_i^+/\chi_j$$

is the relation between the $\chi$-functions $\chi_i^+ = \chi^+ (I_i^+/T_e)$ and $\chi_j = \chi (I_j/T_e)$ for the considered excitation levels: $i$-th ion level and $j$-th atom level, $I_i^+$ and $I_j$ are their respective ionization energies, $g_i$ and $g_j$ are their respective statistical weights and $E_{ij}$ is the energy gap between energy levels of atom and ion.

Equation (4) is different from the equation for the equilibrium case by the factor $\chi_{ij}$ in the end of the right-hand part which can be called the nonequilibrium factor.

On the other hand, concentrations of excited atoms and ions are bound by experimentally obtained spectral line intensities $W$:

$$n_i^+ = n_j W_i A_i \lambda_{jn} / W_j A_j \lambda_{jk},$$

where $A$ is transition probability, $\lambda$ is spectral line wavelength. Eliminating the population relation from this expression, we obtain the formula for determination of $T_e$ from experimental
data:

\[ T_e = E_{ji} \ln^{-1} \left[ \frac{2g_i}{g_j n_e} \left( \frac{2\pi m T_e}{h^2} \right)^{1.5} \frac{W_i A_j}{W_j A_i} \chi_{ij} \lambda_{ij} \right]. \] (7)

Taking into account the nonequilibrium factor \( \chi_{ij} \) in (7) gives the following temperature correction:

\[ \Delta T_e = T(1 + E_{i1}/T\ln(\chi_{ij}))^{-1}. \] (8)

Here \( T \) is the temperature value without nonequilibrium factor taken into account (i.e. at \( \chi_{ij} = 1 \)). Since the factor \( \chi_{ij} \) is under the logarithm, the error of diffusion approach value is weakly dependent on the errors of the \( \chi \)-functions in its expression, being another advantage of this approach. As a result, the electron temperature is:

\[ T_e = T - \Delta T. \]

We’ll give an example of this formula application for spectral lines HeII 468.6 nm and HeI 471.3 nm with respective excited level energies 51.02 eV and 23.6 eV. The values of electron bound energies needed for nonequilibrium factor \( \chi_{ij} \) are \( I_j = 1 \) eV for atom and \( I_j^+ = 3.4 \) eV for ion. The energy gap between them is \( E_{i1} = 52 \) eV. Equilibrium temperatures \( T \) for the electric currents of 200 A and 400 A are 3 eV and 3.3 eV according to our experimental data. Nonequilibrium factor is a slowly increasing function of \( T_e \) and changes only by a few percent in the temperature range of 2.5–3.3 eV: \( \chi_{ij} \approx \text{const} \approx 11 \). Temperature correction gives the following electron temperatures: \( \Delta T = 0.36 \) eV—\( T_e = 2.64 \) eV for 200 A; \( \Delta T = 0.44 \) eV—\( T_e = 2.86 \) eV for 400 A.

These values of \( T_e \) agree well with the ones we obtained from the Doppler width of HeI spectral line at 1083 nm [2].

Excited state population temperature from Saha equations is systematically higher than electron temperature for the nonequilibrium conditions. This is caused by high values of nonequilibrium factor \( \chi_{ij} \approx 11 \gg 1 \) and almost always takes place together with ionization-type nonequilibrium.

High values of \( \chi_{ij} \) mean that atomic excitation levels are much more underpopulated than ion ones. This can be explained by the difference between their electron bounding energies, which is considerably lower for atoms. This behavior can be observed for all plasmas with ion emitting component due the fact that the excited levels of ions have excitation energies along a wide energy range. The difference between highest and lowest excited level energy \( E_i^+ \) for HeII is 13.6 eV.

Figure 2 shows ionization nonequilibrium for excited atoms and ions, deviation from equilibrium energy level population being higher for atoms.

The values of \( T_e \) calculated with formula (7) for different distances from plasma arc axis are shown in figure 3 together with the equilibrium temperatures. The systematic overestimation caused by omitting the nonequilibrium factor is seen to be weakly dependent on \( T_e \) and to have a maximum value of 15%.

Our method gives best results compared to other spectral methods of \( T_e \) determination. This is illustrated by figure 1: the traditional method of \( T_e \) determination from the inclination of the averaging line for the \( \ln(n_k/g_k) \) dependence gives a value that is 5 to 6 times lower: \( T_{id} \approx 0.6 \) eV while taking nonequilibrium into account gives large error and only allows to get a range for possible electron temperatures: \( T_e = 2-5 \) eV.

The proposed spectral method for \( T_e \) determination from atomic and ion line intensities can be improved to exclude the need to use the nonequilibrium factor. This is possible if the electron binding energies of the atomic and ion excited levels are equal. In this case their population logarithms will be located in the same distance from the vertical axis (see figure 2) since \( \chi_{ij} = 1 \) for equal electron bounding energies. From equation (8) \( \Delta T = 0 \) and \( T_e = T \) for these conditions, that is, electron temperature is equal to equilibrium temperature.
Figure 3. Radial distributions of actual and equilibrium electron temperatures for different currents.

Table 1. Pairs of HeI and HeII spectral lines for $T_e$ determination.

| Pair number | Type | $\lambda_0$, nm | $A_{kj}$, $10^{7}$ s$^{-1}$ | $g_k$ | $E_j$, $E_i^+$, eV | $I_j$, $I_i$, eV | $E_{kl}$, eV |
|-------------|------|-----------------|-----------------------------|------|----------------|----------------|--------------|
| 1           | HeI  | 1083.3          | 1.02                        | 9    | 20.96          | 3.62           | 54.64        |
|             | HeII | 468.6           | 14.38                       | 32   | 51.02          | 3.40           |              |
| 2           | HeI  | 706.5           | 2.78                        | 4    | 22.72          | 1.87           | 54.11        |
|             | HeII | 320.3           | 5.50                        | 50   | 52.24          | 2.18           |              |
| 3           | HeI  | 667.8           | 6.38                        | 5    | 23.07          | 1.52           | 54.43        |
|             | HeII | 656.4           | 1.78                        | 72   | 52.91          | 1.51           |              |

A selection of line pairs of atoms and ions with close electron binding energies of emitting excitation levels are given in table 1.

This way the spectral diagnostics of nonequilibrium helium plasma can be based on relations for equilibrium conditions. The proposed spectral method for $T_e$ measurement can be used for all media including spatially-inhomogeneous ones containing both atomic and ion lines in their emission spectra. The condition for applicability of this method is absence of other sources of excited atoms and ions but from inelastic interaction with free electrons having equilibrium (Maxwell’s) distribution over the energies with temperature $T_e$. 
6. Conclusion
Overheated helium arc plasma at atmospheric pressure with strong spatial inhomogeneity is a unique subject for spectral investigation because it combines high electron concentration typical for highly ionized equilibrium plasma and large underpopulation of excited energy levels of atoms and ions typical for weakly ionized nonequilibrium plasma. The task of temperature measurement is solved easily for plasmas of first type but hardly had a reliable method for the second. Combination of these opposite properties is the reason for the distinctions of $T_e$ determination in the considered plasma. $T_e$ measurement becomes possible due to strong ionization of helium and appearance of ion spectral lines in the wavelength range that can be registered. The relation between atomic and ion line intensities is the base for the proposed method of $T_e$ measurement which has accuracy matching that of methods for equilibrium plasma.

References
[1] Biberman L M, Vorobev V S and Yakubov I T 1987 *Kinetics of Nonequilibrium Low-Temperature Plasmas* (Berlin: Springer-Verlag)
[2] Isakaev E K, Chinnov V F, Sargsyan M A and Kavyrshin D I 2013 *High Temp.* **51** 141–146
[3] Jonkers J, Vos H P C, Van Der Mullen J A M and Timmermans E A H 1996 *Spectrochim. Acta, Part B* **51** 457–465
[4] Jonkers J and Van Der Mullen J A M 1999 *J. Quant. Spectrosc. Radiat. Transfer* **61** 703–709
[5] Jonkers J, van de Sande M, Sola A, Gamero A and Van Der Mullen J A M 2003 *Plasma Sources Sci. Technol.* **12** 30–38
[6] Goto M 2003 *J. Quant. Spectrosc. Radiat. Transfer* **76** 331–344
[7] Fujimoto T 1979 *J. Quant. Spectrosc. Radiat. Transfer* **21** 439–455
[8] Amirov A H, Batenin V M, Karlashev A V, Korshunov O V and Chinnov V F 1982 *Dokl. Akad. Nauk SSSR* **266** 1108
[9] Batenin V M, Korshunov O V and Chinnov V F 1986 *Teplofiz. Vys. Temp.* **24** 9
[10] Kavyrshin D I, Chinnov V F and Ageev A G 2015 *J. Phys.: Conf. Ser.* **653** 012115
[11] Isakaev E K, Sinkovich O A, Tyuftyaev A S and Chinnov V F 2010 *High Temp.* **48** 97–125
[12] Lochte-Holtgreven W E 1968 *Plasma Diagnostics* (Amsterdam: Elsevier)
[13] Chinnov V F, Kavyrshin D I, Ageev A G, Korshunov O V and Sargsyan M A 2016 *J. Phys.: Conf. Ser.*