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CONTACT EQUILIBRIUM OF PLASMA SYSTEMS UNDER DIFFERENT ISOLATION CONDITIONS

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ABSTRACT: In this work, the influence of interactions between multi-component plasma systems on their equilibrium compositions is studied. Equilibrium densities of atoms, ions and free electrons in these systems are determined by integration of distribution functions over the space of momentum and summation over electronic energy levels. These functions correspond to the maximum entropy for the combination of systems under different conditions of their interaction. Special attention is given to monatomic plasma mixtures under following situations: 1) the systems may exchange only energy; 2) the systems may exchange energy, electrons and some chemical elements.

KEY WORDS: equilibrium densities of atoms, ions, free electrons, ionization degree, models of plasma systems interactions, statistical description of contact equilibrium of gas systems.

1 INTRODUCTION

The determination of the equilibrium composition of gas systems with physical and chemical processes, and in particular plasma systems, is an important stage of many scientific researches (see, for example, the monographs and the encyclopedias [1–9]). The present study is devoted to the application of statistical physics postulates to solving this kind of problems, like it was done in Ref. [10]. In Ref. [10], the equilibrium states of isolated motionless spatially uniform ionized gas systems were considered in the case when the gas mixtures could be treated as ideal gases even after multiple ionization steps.

In the present paper, the equilibrium states of such gas systems are considered under the various models of the contact interactions between them. Usually, the Massieu–Planck functions are used under these conditions (see, for example, [11–

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15]). In our study, the equilibrium densities of the particles are determined as a result of integration of the distribution functions over the space of momentum and summation over the levels of internal energy. These functions correspond to the maximum entropy for the combination of the interacting systems under certain constraints. The constraints depend on the invariants of collisions between the particles in each system and on the models of the contact interaction between the systems.

Special attention is given to the consideration of monoatomic gas mixtures with multiple ionization, which are assumed enough rarefied to be treated as ideal gases. In such mixtures the total numbers of the nuclei and the electrons (both bound and free) are conserved. Therefore, in the systems under consideration one can use the form of the equilibrium distribution functions which were obtained in the paper [10]. Under these conditions, the evaluation of equilibrium composition in each plasma system is considerably simplified.

During the interactions, the systems exchange their extensive parameters which correspond to the collisions invariants. In the present work, various models of the interactions between the systems are studied in the certain succession. It begins from a very simple thermal interaction. Then the thermal and electronic interactions are taken into account. The existence of the heat-conductive and electro-conductive surfaces can be a foundation for the theoretical consideration of these interactions models between the systems. And finally, along with thermal and electronic interactions, the exchange of some particles which contain the atomic nuclei are taken into account.

The results of these studies can be used for the calculation of the plasma systems equilibrium compositions under the different isolation conditions.

2 CONTACT EQUILIBRIUM OF IDEAL GAS SYSTEMS WITH PHYSICAL AND CHEMICAL PROCESSES

Consider an isolated gas system G which consists of two systems I and II, separated by a fixed surface. If systems I and II are not completely isolated, for the statistical description of system G one can use the common entropy S:

$$S = S_{\rm I} + S_{\rm II}.$$

Taking into account the well known Boltzmann formula for entropy [16] and the fact that entropy is determined with accuracy to a constant, we can present the entropy of each ideal gas system in the form:

(2)
$$S_{\rm I} = k \ln W_1 \Rightarrow k \ln \Delta \Gamma_1 = k \sum_{j'} \ln \Delta \Gamma_{j'}^{(1)},$$

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(3)
$$S_{\rm II} = k \ln W_2 \Rightarrow k \ln \Delta \Gamma_2 = k \sum_{j''} \ln \Delta \Gamma_{j''}^{(2)}$$

Here k is the Boltzmann constant; W_i and $\Delta\Gamma_i$ (i = 1, 2) are respectively thermodynamic probabilities and the numbers of microscopic states which correspond to macroscopic states under consideration of systems I or II; $\Delta\Gamma_{j'}^{(1)}$ and $\Delta\Gamma_{j''}^{(2)}$ are the numbers of microscopic states of the $N_{j'}^{(1)}$ and $N_{j''}^{(2)}$ particles in these systems. These particles are in the definite phase volume, and they are of identical chemical species and have an identical set of quantum numbers which correspond to their internal energy.

If exchange effects are neglected, then using the Stirling formula we can write the expression (1) in the form:

(4)
$$S = \mathbf{k} \bigg[\sum_{j'} \left(N_{j'}^{(1)} \ln s_{j'} - N_{j'}^{(1)} \ln N_{j'}^{(1)} + N_{j'}^{(1)} \right) \\ + \sum_{j''} \left(N_{j''}^{(2)} \ln s_{j''} - N_{j''}^{(2)} \ln N_{j''}^{(2)} + N_{j''}^{(2)} \right) \bigg],$$

where $s_{j'}$ and $s_{j''}$ are the statistical weights (the numbers of possible states) of the particles j' and j''.

The constraints for $N_{j'}^{(1)}$ and $N_{j''}^{(2)}$ depend on existing conservation conditions in systems I and II and on the isolation conditions of these systems. As in Ref. [10], we use the notations $\psi_{j'}^{(\lambda')}(\lambda' = \overline{0, \Lambda'})$ and $\psi_{j''}^{(\lambda'')}(\lambda'' = \overline{0, \Lambda''})$

As in Ref. [10], we use the notations $\psi_{j'}^{(\lambda')}$ ($\lambda' = \overline{0, \Lambda'}$) and $\psi_{j''}^{(\lambda'')}$ ($\lambda'' = \overline{0, \Lambda''}$) for the invariants of any collisions between the particles, and also, $\Psi_{\lambda'}^{(1)}$ and $\Psi_{\lambda''}^{(2)}$ for the summary values of these invariants, in systems I and II (the notations $\psi_{j'}^{(0)} = \varepsilon_{j'}$ and $\psi_{j''}^{(0)} = \varepsilon_{j''}$, and also, $\Psi_0^{(1)} = E_1$ and $\Psi_0^{(2)} = E_2$ are used for the energy of the individual particles and of the whole gas volumes).

If systems I and II are capable of thermal interaction only, then the constraints for $N_{j'}^{(1)}$ and $N_{j''}^{"(2)}$ can be presented in the form

(5)
$$\sum_{j'} N_{j'}^{(1)} \psi_{j'}^{(0)} + \sum_{j''} N_{j''}^{(2)} \psi_{j''}^{(0)} = \Psi_0 = E_{j''}$$

(6)
$$\sum_{j'} N_{j'}^{(1)} \psi_{j'}^{(\lambda')} = \Psi_{\lambda'}^{(1)}, \qquad \lambda' = \overline{1, \Lambda'},$$

(7)
$$\sum_{j''} N_{j''}^{(2)} \psi_{j''}^{(\lambda'')} = \Psi_{\lambda''}^{(2)}, \qquad \lambda'' = \overline{1, \Lambda''}.$$

To determine the equilibrium values $N_{j'}^{(1)}$ and $N_{j''}^{(2)}$, it is necessary to find maximum of function (4) under constraints (5)–(7). After the application of the Lagrange multipliers method, we obtain equilibrium distributions:

(8)
$$N_{j'}^{(1)e} = s_{j'} \exp\left(\gamma_0 \psi_{j'}^{(0)} + \sum_{\lambda'=1}^{\Lambda'} \gamma_{\lambda'}^{(1)} \psi_{j'}^{(\lambda')}\right),$$

(9)
$$N_{j''}^{(2)e} = s_{j''} \exp\left(\gamma_0 \psi_{j''}^{(0)} + \sum_{\lambda''=1}^{\Lambda''} \gamma_{\lambda''}^{(2)} \psi_{j''}^{(\lambda'')}\right).$$

Here $k\gamma_0$, $k\gamma_{\lambda'}^{(1)}$ and $k\gamma_{\lambda''}^{(2)}$ are the Lagrange multipliers which correspond to the constraints (5), (6) and (7).

If the translational energy of particles is described classically or quasi-classically, and their internal energy is assumed quantum, then it is possible to turn from the numbers $N_{j'}^{(1)e}$ (8) and $N_{j''}^{(2)e}$ (9) to the equilibrium distribution functions:

(10)
$$f_{n'}^{(1)e}(\boldsymbol{p}_{n'}) = \frac{s_{n'}}{h^3} \exp\left(\gamma_0 \left(\frac{p_{n'}^2}{2m_{n'}} + \varepsilon_{n'}\right) + \sum_{\lambda'=1}^{\Lambda'} \gamma_{\lambda'}^{(1)} \psi_{n'}^{(\lambda')}\right),$$

(11)
$$f_{n''}^{(2)e}(\boldsymbol{p}_{n''}) = \frac{s_{n''}}{h^3} \exp\left(\gamma_0 \left(\frac{p_{n''}^2}{2m_{n''}} + \varepsilon_{n''}\right) + \sum_{\lambda''=1}^{\Lambda''} \gamma_{\lambda''}^{(2)} \psi_{n''}^{(\lambda'')}\right).$$

Here the subscripts n' and n'' correspond to the chemical species and the sets of quantum numbers which specify the internal energy of the particles; h is Planck constant; $m_{n'}$ and $m_{n''}$, $p_{n'}$ and $p_{n''}$, $\varepsilon_{n'}$ and $\varepsilon_{n''}$, $s_{n'}$ and $s_{n''}$ are the masses, momenta, internal energies, statistical weights of the particles in systems I and II; $\psi_{n'}^{(\lambda')}$ and $\psi_{n''}^{(\lambda'')}$ are collision invariants which do not depend on the momentum.

In Ref. [10] it was noted that the distribution functions in form (10) and (11) can also be obtained from the kinetic equations for local equilibrium flows of gases with physical and chemical processes (see, for example, the papers [17, 18] and the monographs [15, 19, 20]).

In the equilibrium, the states of gas systems are spatially uniform. Therefore, the normalization conditions have the form:

(12)
$$V_{1} \sum_{n'} \int f_{n'}^{(1)e} \left(\boldsymbol{p}_{n'} \right) \left(\frac{p_{n'}^{2}}{2m_{n'}} + \varepsilon_{n'} \right) d\boldsymbol{p}_{n'} + V_{2} \sum_{n''} \int f_{n''}^{(2)e} \left(\boldsymbol{p}_{n''} \right) \left(\frac{p_{n''}^{2}}{2m_{n''}} + \varepsilon_{n''} \right) d\boldsymbol{p}_{n''} = E,$$

(13)
$$V_1 \sum_{n'} \psi_{n'}^{(\lambda')} \int f_{n'}^{(1)e} \left(\boldsymbol{p}_{n'} \right) d\boldsymbol{p}_{n'} = \Psi_{\lambda'}^{(1)}, \qquad \lambda' = \overline{1, \Lambda'},$$

(14)
$$V_2 \sum_{n''} \psi_{n''}^{(\lambda'')} \int f_{n''}^{(2)e} \left(\boldsymbol{p}_{n''} \right) d\boldsymbol{p}_{n''} = \Psi_{\lambda''}^{(2)}, \qquad \lambda'' = \overline{1, \Lambda''},$$

where V_1 and V_2 are the gas volumes of systems I and II. The coefficients γ_0 , $\gamma_{\lambda'}^{(1)}$ ($\lambda' = \overline{1, \Lambda'}$) and $\gamma_{\lambda''}^{(2)}$ ($\lambda'' = \overline{1, \Lambda''}$) are determined from equations (12)-(14).

Relation (12) enables to obtain the equality $\gamma_0 = -1/(kT)$, where T is the thermodynamic temperature, identical in systems I and II.

If systems I and II can exchange not only energy, but also the some collision invariants $\psi_{j'}^{(\lambda)}$ and $\psi_{j''}^{(\lambda)}$ ($\lambda = \overline{1, \lambda_*}$), then the constraints for $N_{j'}^{(1)}$ and $N_{j''}^{(2)}$ contain, along with relation (5), the conditions:

(15)
$$\sum_{j'} N_{j'}^{(1)} \psi_{j'}^{(\lambda)} + \sum_{j''} N_{j''}^{(2)} \psi_{j''}^{(\lambda)} = \Psi_{\lambda}, \quad \lambda = \overline{1, \lambda_*},$$

and also, relations (6) for $\lambda' = \overline{\lambda_* + 1, \Lambda'}$, and (7) for $\lambda'' = \overline{\lambda_* + 1, \Lambda''}$.

In this situation, after the application of the Lagrange method, we obtain equilibrium distributions:

(16)
$$N_{j'}^{(1)e} = s_{j'} \exp\left(\sum_{\lambda=0}^{\lambda_*} \gamma_\lambda \psi_{j'}^{(\lambda)} + \sum_{\lambda'=\lambda_*+1}^{\Lambda'} \gamma_{\lambda'}^{(1)} \psi_{j'}^{(\lambda')}\right),$$

(17)
$$N_{j''}^{(2)e} = s_{j''} \exp\left(\sum_{\lambda=0}^{\lambda_*} \gamma_\lambda \psi_{j''}^{(\lambda)} + \sum_{\lambda''=\lambda_*+1}^{\Lambda''} \gamma_{\lambda''}^{(2)} \psi_{j''}^{(\lambda'')}\right),$$

where $k\gamma_{\lambda}$ are the Lagrange multipliers which correspond to constraints (5) and (15).

Under the classical or quasi-classical description of the translational energy, the equilibrium distribution functions have the form:

(18)
$$f_{n'}^{(1)e} = \frac{s_{n'}}{h^3} \exp\left(\gamma_0 \left(\frac{p_{n'}^2}{2m_{n'}} + \varepsilon_{n'}\right) + \sum_{\lambda=1}^{\lambda_*} \gamma_\lambda \psi_{n'}^{(\lambda)} + \sum_{\lambda'=\lambda_*+1}^{\Lambda'} \gamma_{\lambda'}^{(1)} \psi_{n'}^{(\lambda')}\right),$$
(19)
$$f_{n''}^{(2)e} = \frac{s_{n''}}{h^3} \exp\left(\gamma_0 \left(\frac{p_{n''}^2}{2m_{n''}} + \varepsilon_{n''}\right) + \sum_{\lambda=1}^{\lambda_*} \gamma_\lambda \psi_{n''}^{(\lambda)} + \sum_{\lambda'=\lambda_*+1}^{\Lambda''} \gamma_{\lambda''}^{(2)} \psi_{n''}^{(\lambda'')}\right).$$

The normalization conditions for functions (18) and (19) contain, along with (12), the relations:

(20)
$$V_1 \sum_{n'} \psi_{n'}^{(\lambda)} \int f_{n'}^{(1)e} d\mathbf{p}_{n'} + V_2 \sum_{n''} \psi_{n''}^{(\lambda)} \int f_{n''}^{(2)e} d\mathbf{p}_{n''} = \Psi_{\lambda}, \qquad \lambda = \overline{1, \lambda_*},$$

complemented with relations (13) for $\lambda' = \overline{\lambda_* + 1, \Lambda'}$ and relations (14) for $\lambda'' = \overline{\lambda_* + 1, \Lambda''}$. Temperature *T*, coefficients γ_{λ} ($\lambda = \overline{1, \lambda_*}$) identical for two systems, and also coefficients $\gamma_{\lambda'}^{(1)}$ ($\lambda = \overline{\lambda_* + 1, \Lambda'}$) and $\gamma_{\lambda''}^{(2)}$ ($\lambda = \overline{\lambda_* + 1, \Lambda''}$) are determined from these relations.

The distribution functions (18) and (19) allow us to simplify the description of contact interactions between gas systems with any physical and chemical processes.

Relations (12) and (20) determine the connection between extensive parameters $(\Psi_0 = E \text{ and } \Psi_\lambda, \lambda = \overline{1, \lambda_*})$ and intensive parameters $(\gamma_0 = -1/(kT) \text{ and } \gamma_\lambda, \lambda = \overline{1, \lambda_*})$.

In the following sections, the different interactions between the plasma systems are studied.

3 EQUILIBRIUM COMPOSITION OF IONIZED GAS SYSTEMS UNDER THERMAL INTERACTION

Consider the situation, when each of systems I and II is an ionized mixture of monoatomic gases. These mixtures are assumed enough rarefied to be treated as ideal gases. They contain the particles of various chemical species: $k' = 1, 2, ..., k'_*$ (system I) and $k'' = 1, 2, ..., k''_*$ (system II), and free electrons *e*.

Hypothetically, in system I one can find neutral atoms $A_{k'0}$ and ions $A_{k'c}$ with a charge $c = +1, +2, \ldots, +N(k')$, and in system II: atoms $A_{k''0}$ and ions $A_{k''c}$ with a charge $c = +1, +2, \ldots, +N(k'')$. N(k') and N(k'') are the serial numbers of elements $A_{k'}$ and $A_{k''}$ in the periodic system. Every particle $A_{k'c}$ contains nucleus $A_{k'}^*$ and (N(k') - c) electrons, and every particle $A_{k''c}$ contains nucleus $A_{k''}^*$ and (N(k'') - c) electrons.

The total energy, the numbers of each kind of nuclei and the electrons are conserved under any collisions.

In this section we consider the systems with thermal interaction when the constraints (5)–(7) are satisfied. Relation (5) corresponds to the conservation of the total energy in the combination of the systems I and II. Relations (6) correspond to the conservation of the nuclei $A_{k'}^*$ and the electrons (both bound and free) in system I. Relations (7) correspond to the conservation of the nuclei $A_{k''}^*$ and all electrons in system II.

Accordingly, the equilibrium distributions, which correspond to the entropy maximum, can be presented in the form (8) and (9).

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In the spatially uniform gas systems with classical or quasi-classical description of the particles translational energy, one can turn to the distribution functions (10) and (11). In the ionized gas systems under consideration, these equilibrium distribution functions can be written in the form [10]:

(21)
$$f_{k'ci}^{(1)}(\boldsymbol{p}_{k'c}) = \frac{s_{k'ci}}{h^3} \exp\left(-\frac{p_{k'c}^2/(2m_{k'c}) + \varepsilon_{k'ci}}{kT} + \gamma_{k'}^{(1)} + \gamma_e^{(1)}(N(k') - c)\right),$$
$$i = \left\{i_{c+1}, \dots, i_{N(k')}\right\}, \quad c = \overline{0, N(k')}, \quad k' = \overline{1, k'_*};$$

(22)
$$f_e^{(1)}(\boldsymbol{p}_e) = \frac{1}{h^3} \exp\left(-\frac{p_e^2/(2m_e)}{kT} + \gamma_e^{(1)}\right)$$

and

(23)
$$f_{k''ci}^{(2)}(\boldsymbol{p}_{k''c}) = \frac{s_{k''ci}}{h^3} \exp\left(-\frac{p_{k''c}^2/(2m_{k''c}) + \varepsilon_{k''ci}}{kT} + \gamma_{k''}^{(2)} + \gamma_e^{(2)}(N(k'') - c)\right),$$
$$i = \left\{i_{c+1}, \dots, i_{N(k'')}\right\}, \quad c = \overline{0, N(k'')}, \quad k'' = \overline{1, k''_*};$$

(24)
$$f_e^{(2)}(\boldsymbol{p}_e) = \frac{1}{h^3} \exp\left(-\frac{p_e^2/(2m_e)}{kT} + \gamma_e^{(2)}\right).$$

Here $f_{k'ci}^{(1)}$ and $f_{k''ci}^{(2)}$ are the distribution functions of the particles $A_{k'c}$ and $A_{k''c}$ with internal electronic energy $\varepsilon_{k'ci}$ and $\varepsilon_{k''ci}$ in systems I and II; $f_e^{(1)}$ and $f_e^{(2)}$ are the distribution functions of free electrons in systems I and II; $m_{k'c}$, $m_{k''c}$ and m_e , and $p_{k'c}$, $p_{k''c}$ and p_e are the masses and momenta of the corresponding particles; $\varepsilon_{k'ci}$ and $\varepsilon_{k''ci}$ are their internal energy which can be presented in the form:

(25)
$$\varepsilon_{k'ci} = \sum_{l=c+1}^{N(k')} (\varepsilon_{i_l}^{(k'c)} - I_l^{(k'c)}),$$
$$i_l = \overline{0, i_l^*(k'c)}, \quad c = \overline{0, N(k') - 1}, \quad \varepsilon_{k'N(k')i} = 0, \qquad k' = \overline{1, k'_*};$$

(26)
$$\varepsilon_{k''ci} = \sum_{l=c+1}^{N(k'')} (\varepsilon_{i_l}^{(k''c)} - I_l^{(k''c)}),$$
$$i_l = \overline{0, i_l^*(k''c)}, \quad c = \overline{0, N(k'') - 1}, \quad \varepsilon_{k''N(k'')i} = 0, \qquad k'' = \overline{1, k''_*},$$

where i_l is the electronic energy level l, which changes from $i_l = 0$ to i_l^* . In the ground state $\varepsilon_0 = 0$, whereas on the upper levels $\varepsilon_{i_l^*} \approx I_l^{(k'c)}$ in the particle $A_{k'c}$ and $\varepsilon_{i_l^*} \approx I_l^{(k''c)}$ in the particle $A_{k''c}$ ($I_l^{(k'c)}$ and $I_l^{(k''c)}$ are the ionization potentials).

Coefficients $\gamma_{k'}^{(1)}$ and $\gamma_{k''}^{(2)}$ are connected to the collision invariants which are related to the conservation of the nuclei $A_{k'}^*$ and $A_{k''}^*$; $\gamma_e^{(1)}$ and $\gamma_e^{(2)}$ are connected to the invariants which are related to the conservation of the electrons.

As a result of thermal interaction between the systems, coefficient $\gamma_0 = -1/(kT)$ takes identical value in systems I and II.

One can obtain equilibrium concentrations $n_{k'c}^{(1)}$ and $n_e^{(1)}$ of particles $A_{k'c}$ and free electrons in system I or concentrations $n_{k''c}^{(2)}$ and $n_e^{(2)}$ of particles $A_{k''c}$ and free electrons in system II, as a result of integration over the space of momentum and summation over the electronic energy levels of functions (21) and (22) or (23) and (24).

Thus, one can write

(27)
$$n_{k'c}^{(1)} = Z_{k'c}(T) \exp\left(\gamma_{k'}^{(1)} + \gamma_e^{(1)}\left(N(k') - c\right)\right),$$
$$c = \overline{0, N(k')}, \ k' = \overline{1, k'_*};$$

(28)
$$n_e^{(1)} = Z_e(T) \exp(\gamma_e^{(1)});$$

(29)
$$n_{k''c}^{(2)} = Z_{k''c}(T) \exp\left(\gamma_{k''}^{(2)} + \gamma_e^{(2)}\left(N(k'') - c\right)\right),$$
$$c = \overline{0, N(k'')}, \ k'' = \overline{1, k''_*};$$

(30)
$$n_e^{(2)} = Z_e(T) \exp(\gamma_e^{(2)})$$

Here, $Z_{k'c}(T)$, $Z_{k''c}(T)$ and $Z_e(T)$ are the partition functions:

(31)
$$Z_{k'c}(T) = Z_{k'c}^{\mathrm{tr}}(T) \cdot Z_{k'c}^{\mathrm{int}}(T), \quad c = \overline{0, N(k')}, \quad k' = \overline{1, k'_*},$$

(32)
$$Z_{k''c}(T) = Z_{k''c}^{tr}(T) \cdot Z_{k''c}^{int}(T), \quad c = \overline{0, N(k'')}, \quad k'' = \overline{1, k''_*},$$

$$(33) Z_e(T) = Z_e^{\rm tr}(T).$$

For the calculation of the partition functions $Z_{k'c}^{\text{int}}$ or $Z_{k''c}^{\text{int}}$ one may use formulae (25) and (26) and the finite sets of electronic levels from [21]. Also, one may use the partition functions of the atoms and ions, which were calculated earlier (see, for example, [9, 22, 23]).

In Ref. [10] it was noted that concentrations (27) and (28) or (29) and (30) satisfy the Saha equations [24] for the arbitrary values of T, γ_k ($k = \overline{1, k_*}$) and γ_e .

To find the parameters $\gamma_{k'}^{(1)}$ $(k' = \overline{1, k'_*})$ and $\gamma_e^{(1)}$ in the expressions (27) and (28) or $\gamma_{k''}^{(2)}$ $(k'' = \overline{1, k''_*})$ and $\gamma_e^{(2)}$ in (29) and (30) it is necessary to solve the set of equations:

(34)
$$\sum_{c=0}^{N(k')} n_{k'c}^{(1)} = \widetilde{n}_{k'}^{(1)}, \quad k' = \overline{1, k'_{*}},$$

(35)
$$\sum_{k'=1}^{k'_*} \sum_{c=0}^{N(k')} n_{k'c}^{(1)} \left(N(k') - c \right) + n_e^{(1)} = \widetilde{n}_e^{(1)}$$

or

(36)
$$\sum_{c=0}^{N(k'')} n_{k''c}^{(2)} = \widetilde{n}_{k''}^{(2)}, \quad k'' = \overline{1, k''_*},$$

(37)
$$\sum_{k''=1}^{\kappa_*} \sum_{c=0}^{N(\kappa)} n_{k''c}^{(2)} \left(N(k'') - c \right) + n_e^{(2)} = \widetilde{n}_e^{(2)}.$$

The values $\tilde{n}_{k'}^{(1)}$ and $\tilde{n}_e^{(1)}$ correspond to total numbers of the nuclei $A_{k'}^*$ and the electrons e (both bound and free) in the unit volume of system I; $\tilde{n}_{k''}^{(2)}$ and $\tilde{n}_e^{(2)}$ correspond to total numbers of the nuclei $A_{k''}^*$ and all electrons in the unit volume of system II. These values are known if the initial compositions of the systems I and II are known.

One can notice that the conservation of every chemical element's mass and the electric charges in unit volume of systems I or II is the consequences of relations (34) and (35) or (36) and (37).

If temperature T of the supplementary system II is known, then temperature of system I is also known. The problem of the determination of the system I equilibrium composition is reduced to the problem which was solved in Ref. [10].

For the calculation of system I and II equilibrium compositions one can introduce the notations (see Ref. [10]):

(38)
$$e^{\gamma_{k'}^{(1)}} = x_{k'}^{(1)}, \quad k' = \overline{1, k'_*}; \qquad e^{\gamma_e^{(1)}} = y_1$$

and

(39)
$$e^{\gamma_{k''}^{(2)}} = x_{k''}^{(2)}, \quad k'' = \overline{1, k''_{*}}; \qquad e^{\gamma_{e}^{(2)}} = y_2.$$

It allows us to write expressions (27)-(30) in the form

(40)
$$n_{k'c}^{(1)} = Z_{k'c}(T)x_{k'}^{(1)}y_1^{N(k')-c}, \quad k' = \overline{1,k'_*}, \quad c = \overline{0,N(k')};$$

(41)
$$n_e^{(1)} = Z_e(T)y_1$$

and

(42)
$$n_{k''c}^{(2)} = Z_{k''c}(T) x_{k''}^{(2)} y_2^{N(k'')-c}, \quad k'' = \overline{1, k_*''}, \quad c = \overline{0, N(k'')};$$

(43)
$$n_e^{(2)} = Z_e(T)y_2.$$

For the determination of the parameters $x_{k'}^{(1)}$, y_1 and $x_{k''}^{(2)}$, y_2 we have the set of equations:

(44)
$$x_{k'}^{(1)} \sum_{c=0}^{N(k')} Z_{k'c}(T) y_1^{N(k')-c} = \widetilde{n}_{k'}^{(1)}, \quad k' = \overline{1, k'_*},$$

(45)
$$\sum_{k'=1}^{k'_*} x_{k'}^{(1)} \sum_{c=0}^{N(k')} Z_{k'c}(T) y_1^{N(k')-c} \left(N(k') - c \right) + Z_e(T) y_1 = \widetilde{n}_e^{(1)}$$

and

(46)
$$x_{k''}^{(2)} \sum_{c=0}^{N(k'')} Z_{k''c}(T) y_2^{N(k'')-c} = \widetilde{n}_{k''}^{(2)}, \quad k'' = \overline{1, k''_*},$$

(47)
$$\sum_{k''=1}^{k''_*} x_{k''}^{(2)} \sum_{c=0}^{N(k'')} Z_{k''c}(T) y_2^{N(k'')-c} \left(N(k'') - c \right) + Z_e(T) y_2 = \widetilde{n}_e^{(2)}.$$

From equations (44) and (46) we obtain the expressions:

(48)
$$x_{k'}^{(1)} = \frac{\widetilde{n}_{k'}^{(1)}}{\Phi_{k'}(T, y_1)}, \quad k' = \overline{1, k'_*}, \quad x_{k''}^{(2)} = \frac{\widetilde{n}_{k''}^{(2)}}{\Phi_{k''}(T, y_2)}, \quad k'' = \overline{1, k''_*},$$

where

(49)
$$\Phi_{k'}(T,y_1) = \sum_{c=0}^{N(k')} Z_{k'c}(T) y_1^{N(k')-c}, \quad \Phi_{k''}(T,y_2) = \sum_{c=0}^{N(k'')} Z_{k''c}(T) y_2^{N(k'')-c}.$$

We can interpret expressions (49) as the partition functions for chemical elements $A_{k'}$ and $A_{k''}$.

After the substitution expressions (48) to equations (45) and (47) we obtain the equations:

(50)
$$f_1(T, y_1) = \widetilde{n}_e^{(1)}, \quad f_2(T, y_2) = \widetilde{n}_e^{(2)}$$

for the determination of y_1 and y_2 , where

(51)
$$f(T,y) = \sum_{k=1}^{k_*} \frac{\widetilde{n}_k}{\Phi_k(T,y)} \sum_{c=0}^{N(k)} (N(k)-c) Z_{kc}(T) y^{N(k)-c} + Z_e(T) y.$$

In Ref. [10] it was proved that equations (50) have one and only one positive solution at any temperature T.

Just as it was expected, under thermal interaction between the systems I and II, the equilibrium composition of system I does not depend on the system II composition.

One can consider that the equilibrium state of system I is a consequence of its thermal ionization. The method for the calculation of the multi-component plasma equilibrium composition under these conditions was proposed in Ref. [10]. The examples of this method application for the calculations of the equilibrium composition of the thermally ionized nitrogen under the different values of temperature and the initial density are given in Ref. [25].

4 EQUILIBRIUM COMPOSITION OF IONIZED GAS SYSTEMS UNDER THERMAL AND ELECTRONIC INTERACTIONS

Consider the same ionized gas systems, separated by a fixed surface, as in Section 3. However, now these systems can exchange not only energy but also electrons. For the calculation of these systems' equilibrium compositions it is necessary to find maximum of the entropy for the combination of systems I and II under the definite set of the constraints. In this section such set contains relation (5) and one of relations (15). These relations correspond to the conservation of the total energy and the total number the electrons (both bound and free) in the combination of systems I and II. Also, this set contains relations (6) and (7) which correspond to the conservation of the nuclei $A_{k'}^*$ in system I and $A_{k''}^*$ in system II.

In this situation, the equilibrium distributions can be presented in the form (16) and (17). There are identical coefficients $\gamma_0 = -1/(kT)$ before the energy and γ_e before the electrons numbers in the particles of systems I and II. Under these conditions equilibrium distribution functions (18) and (19) can be written in the form:

(52)
$$f_{k'ci}^{(1)}(\boldsymbol{p}_{k'c}) = \frac{s_{k'ci}}{h^3} \exp\left(-\frac{p_{k'c}^2/(2m_{k'c}) + \varepsilon_{k'ci}}{kT} + \gamma_{k'}^{(1)} + \gamma_e\left(N(k') - c\right)\right),$$
$$i = \left\{i_{c+1}, \dots, i_{N(k')}\right\}, \quad c = \overline{0, N(k')}, \quad k' = \overline{1, k'_*};$$

(53)
$$f_e^{(1)}(\boldsymbol{p}_e) = \frac{1}{h^3} \exp\left(-\frac{p_e^2/(2m_e)}{kT} + \gamma_e\right);$$

and

(54)
$$f_{k''ci}^{(2)}(\boldsymbol{p}_{k''c}) = \frac{s_{k''ci}}{h^3} \exp\left(-\frac{p_{k''c}^2/(2m_{k''c}) + \varepsilon_{k''ci}}{kT} + \gamma_{k''}^{(2)} + \gamma_e(N(k'') - c)\right),$$
$$i = \left\{i_{c+1}, \dots, i_{N(k'')}\right\}, \quad c = \overline{0, N(k'')}, \quad k'' = \overline{1, k''_*};$$

(55)
$$f_e^{(2)}(\boldsymbol{p}_e) = \frac{1}{h^3} \exp\left(-\frac{p_e^2/(2m_e)}{kT} + \gamma_e\right).$$

After the integration of functions (52)–(55) over the spaces of momentum and the summation over the levels of the internal energy we obtain the expressions:

(56)
$$n_{k'c}^{(1)} = Z_{k'c}(T) \exp\left(\gamma_{k'}^{(1)} + \gamma_e(N(k') - c)\right), \ c = \overline{0, N(k')}, \ k' = \overline{1, k'_*},$$

(57)
$$n_{k''c}^{(2)} = Z_{k''c}(T) \exp\left(\gamma_{k''}^{(2)} + \gamma_e(N(k'') - c)\right), \ c = \overline{0, N(k'')}, \ k'' = \overline{1, k''_*},$$

(58)
$$n_e^{(1)} = n_e^{(2)} = Z_e(T) \exp \gamma_e.$$

or

(59)
$$n_{k'c}^{(1)} = Z_{k'c}(T) x_{k'}^{(1)} y^{N(k')-c}, \quad c = \overline{0, N(k')}, \ k' = \overline{1, k'_*},$$

(60)
$$n_{k''c}^{(2)} = Z_{k''c}(T) x_{k''}^{(2)} y^{N(k'')-c}, \quad c = \overline{0, N(k'')}, \ k'' = \overline{1, k_*''},$$

(61)
$$n_e^{(1)} = n_e^{(2)} = Z_e(T)y,$$

if to use the notations (38) and (39).

Thus, under the exchanges of the energy and electrons between the systems, in the equilibrium there are the identical densities of free electrons. If we know temperature T and density $n_e^{(2)}$ of free electrons in test system II, then we know temperature T and density $n_e^{(1)}$ of free electrons in system I.

Formulae (48) and (59), (60) allow us to calculate the ionization degrees of chemical elements $A_{k'}$ in system I and $A_{k''}$ in system II:

(62)
$$\frac{n_{k'c}^{(1)}}{\widetilde{n}_{k'}^{(1)}} = \frac{Z_{k'c}(T) y^{N(k')-c}}{\Phi_{k'}(T, y)}, \qquad c = \overline{0, N(k')}, \quad k' = \overline{1, k'_*},$$

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and

(63)
$$\frac{n_{k''c}^{(2)}}{\widetilde{n}_{k''}^{(2)}} = \frac{Z_{k''c}(T) y^{N(k'')-c}}{\Phi_{k''}(T,y)}, \qquad c = \overline{0, N(k'')}, \quad k'' = \overline{1, k''_*}.$$

It should be noted that in the situation, when in systems I and II the identical chemical elements A_k ($k = \overline{1, k_*}$) are present, then the equalities

(64)
$$\frac{n_{kc}^{(1)}}{\widetilde{n}_k^{(1)}} = \frac{n_{kc}^{(2)}}{\widetilde{n}_k^{(2)}}, \qquad c = \overline{0, N(k)}, \quad k = \overline{1, k_*},$$

are correct and the ionization degrees of these elements coincide in systems I and II.

5 EQUILIBRIUM COMPOSITION OF IONIZED GAS SYSTEMS UNDER EXCHANGES OF ENERGY, ELECTRONS AND SOME CHEMICAL ELEMENTS

In this section, consider the same ionized gas systems as in Section 3 and 4, but now some kinds of heavy particles A_k $(k = \overline{1, k_*})$ can pass through separated surface, along with energy and electrons. For the determination of the systems I and II equilibrium compositions, it is necessary to find maximum of entropy (4) constrained by the conservation of total energy (5) and the set of conditions (15) which correspond to the conservation of the total numbers of electrons and the nuclei A_k^* $(k = \overline{1, k_*})$. Also, it is necessary to take into account relations (6) and (7) which correspond to the conservation of the nuclei $A_{k'}^*$ $(k' = \overline{k_* + 1, k'_*})$ in system I and $A_{k''}^*$ $(k'' = \overline{k_* + 1, k''_*})$ in system II.

Under these conditions in distributions (16) and (17), the identical coefficients γ_0 , γ_k ($k = \overline{1, k_*}$) and γ_e are present. After the transition to distribution functions (18) and (19), we can write

(65)
$$f_{kci}^{(1)}(\boldsymbol{p}_e) = f_{kci}^{(2)}(\boldsymbol{p}_e) = \frac{s_{kci}}{h^3} \exp\left(-\frac{p_{kc}^2/(2m_{kc}) + \varepsilon_{kci}}{kT} + \gamma_k + \gamma_e(N(k) - c)\right),$$
$$c = \overline{0, N(k)}, \quad k = \overline{1, k_*}, \quad i = \left\{i_{c+1}, \dots, i_{N(k)}\right\};$$

(66)
$$f_e^{(1)}(\boldsymbol{p}_e) = f_e^{(2)}(\boldsymbol{p}_e) = \frac{1}{h^3} \exp\left(-\frac{p_e^2/(2m_e)}{kT} + \gamma_e\right);$$

(67)
$$f_{k'ci}^{(1)}(\boldsymbol{p}_e) = \frac{s_{k'ci}}{h^3} \exp\left(-\frac{p_{k'c}^2/(2m_{k'c}) + \varepsilon_{k'ci}}{kT} + \gamma_{k'}^{(1)} + \gamma_e(N(k') - c)\right), \\ c = \overline{0, N(k')}, \quad k' = k_* + 1, \dots, k'_*, \quad i = \left\{i_{c+1}, \dots, i_{N(k')}\right\};$$

(68)
$$f_{k''ci}^{(2)}(\boldsymbol{p}_e) = \frac{s_{k''ci}}{h^3} \exp\left(-\frac{p_{k''c}^2/(2m_{k''c}) + \varepsilon_{k''ci}}{kT} + \gamma_{k''}^{(2)} + \gamma_e(N(k'') - c)\right),$$

$$c = \overline{0, N(k'')}, \quad k'' = k_* + 1, \dots, k_*'', \quad i = \left\{i_{c+1}, \dots, i_{N(k'')}\right\}.$$

In systems I and II, the equilibrium densities of free electrons e have the identical values (see expressions (58) or (61)). For the equilibrium densities of the particles A_{kc} in systems I and II one can write the equalities:

(69)
$$n_{kc}^{(1)} = n_{kc}^{(2)} = Z_{kc}(T) \exp\left(\gamma_k + \gamma_e(N(k) - c)\right) = Z_{kc}(T) x_k y^{N(k) - c},$$

 $c = \overline{0, N(k)}, \ k = \overline{1, k_*}.$

If we know the equilibrium densities of the particles A_{kc} ($c = 0, N(k), k = \overline{1, k_*}$)

in supplementary system II, then we know these densities in system I. The equilibrium densities $n_{k'c}^{(1)}$ and $n_{k''c}^{(2)}$ of the particles $A_{k'c}$ $(k' = \overline{k_* + 1, k'_*})$ and $A_{k''c}$ $(k'' = \overline{k_* + 1, k'_*})$ which cannot pass through separated surface have different values (see (56) and (57)).

However, if some of these particles $A_{k'c}$ $(c = \overline{0, N(k')})$ and $A_{k''c}$ $(c = \overline{0, N(k'')})$ correspond to identical chemical elements $A_{k'} = A_{k''}$, then the equalities (64) are satisfied. The ionization degrees of these elements coincide.

Remark. If at any situation under consideration (see Sections 3, 4, 5), it is known that the gas mixture I contains the ions $A_{k'c}$ with a charge of no greater than $c_*(k') < N(k')$ and mixture II contains the ions $A_{k''c}$ with a charge of no greater than $c_*(k'') < N(k'')$, then the conservation conditions of the nuclei $A_{k'}^*$ and $A_{k''}^*$ can be substituted to the conservation conditions of the ions $A_{c_*(k')}$ and $A_{c_*(k'')}$. The conservation conditions of all electrons (both bound and free) are substituted to the conservation conditions of the electrons (both bound and free). The method of the evaluation of the ionized gas systems equilibrium composition is, therefore, simplified (see, for example, [25]).

NUMERICAL ILLUSTRATIONS 6

Consider the situation when our system I is a multiply ionized monoatomic nitrogen plasma. The calculation results of the equilibrium compositions of such thermally ionized systems with the application of the method which was proposed in Ref. [10] were adduced in Ref. [10, 25].

As in Ref. [10], we limit oneself to the consideration of the nitrogen plasma with four-order ionization. In this case the numbers of the nitrogen ions N^{++++} with a charge +4 and of the electrons (both bound and free) are conserved under any collisions. Formulae (40) and (41) can be written in the form

(70)
$$\begin{aligned} n_0^{(1)} &= Z_0(T)x^{(1)}y_1^4, \qquad n_1^{(1)} &= Z_1(T)x^{(1)}y_1^3, \qquad n_2^{(1)} &= Z_2(T)x^{(1)}y_1^2, \\ n_3^{(1)} &= Z_3(T)x^{(1)}y_1, \qquad n_4^{(1)} &= Z_4(T)x^{(1)}, \qquad n_e^{(1)} &= Z_e(T)y_1. \end{aligned}$$

Here $n_0^{(1)}$, $n_1^{(1)}$, $n_2^{(1)}$, $n_3^{(1)}$, $n_4^{(1)}$ are the densities of the nitrogen atoms and ions with the charges c = +1, +2, +3, +4. Factor $x^{(1)}$ shows to the presence of the nitrogen ion with charge +4 in these particles.

Figure 1 in Ref. [10] shows the temperature dependence of the system I equilibrium composition under its thermal ionization. In the present paper, we use this figure for the illustration of the influence of the interaction models between systems I and II on their equilibrium composition and the ionization degree.



Fig. 1: Equilibrium composition of system I. Curve 1 corresponds to $n_0^{(I)}/\tilde{n}_{\rm I}$, 2 — to $n_1^{(I)}/\tilde{n}_{\rm I}$, 3 — to $n_2^{(I)}/\tilde{n}_{\rm I}$, 4 — to $n_3^{(I)}/\tilde{n}_{\rm I}$, 5 — to $n_4^{(I)}/\tilde{n}_{\rm I}$, 6 — to $n_e^{(I)}/N_L$.

Here \tilde{n}_{I} is equilibrium density of ions N^{++++} which is equal to the total density of nitrogen atoms and ions in system I; N_{L} is Loschmidt number.

It should be noted that the relative values $n_c^{(I)}/\tilde{n}_I$ (c = 0, 1, 2, 3, 4) determine the ionization degree of the nitrogen atoms in system I.

1. Let only thermal interaction be able between systems I and II.

This situation is described in Section 3. Identical values of temperature T are settled in systems I and II. Equilibrium density \tilde{n}_{I} of ions N^{++++} is equal to the initial density $\tilde{n}_{I}^{(0)}$ of the nitrogen particles. Free electrons *e* appear in system I only from the ionization of the nitrogen atoms and ions.

Under these conditions, curve 6 shows the temperature dependence of the free electron density in system I, and curves 1–5 show the dependence on the temperature T of the relative values $n_c^{(1)}/\tilde{n}_{\rm I}$ (c = 0, 1, 2, 3, 4) when $\tilde{n}_{\rm I} = n_{\rm I}^{(0)} = N_L$. The equilibrium composition of system I does not depend on the system II composition.

2. Let systems I and II be able to exchange energy and electrons.

This situation is described in Section 4. Identical values of temperature T and of electronic coefficient γ_e (or $y = e^{\gamma_e}$) are settled in systems I and II. Again, equilibrium density \tilde{n}_I of ions N^{++++} is equal to their initial density $\tilde{n}_I^{(0)}$. The presence of free electrons in system I is connected with the ionization of the nitrogen particles in this system and an electronic exchange between systems I and II.

Under these conditions, from relations (58) and (61) one can see that in equilibrium, the densities of free electrons have the identical values in systems I and II. Curve 6 shows the temperature dependence of these densities.

From relations (62) one can see that the relative values $n_c^{(1)}/\tilde{n}_{\rm I}$ depend only on the temperature T and factor y. Therefore, curves 1–5 show the temperature dependencies of these relative values under the arbitrary densities $\tilde{n}_{\rm I} = \tilde{n}_{\rm I}^{(0)}$.

3. Let systems I and II be able to exchange energy, electrons, and also nitrogen atoms and ions.

This situation is described in Section 5. We obtain identical values for temperature T, electronic coefficient γ_e (or $y = e^{\gamma_e}$) and factor γ before the collision invariants which correspond to the conservation of the nitrogen ions with charge +4 (or $x = e^{\gamma}$) in systems I and II. From formulae (69) one can see that the equilibrium densities of the nitrogen atoms and ions, and also of free electrons coincide in system I and II. Under these conditions $\tilde{n}_{\rm I} \neq \tilde{n}_{\rm I}^{(0)}$ but $\tilde{n}_{\rm I} = \tilde{n}_{\rm II}$.

Curve 6 shows the dependence of the free electrons densities on temperature T in systems I and II.

Curves 1–5 show the temperature dependence of the relative values $n_c^{(1)}/\tilde{n}_{\rm I}$ (c = 0, 1, 2, 3, 4), which define the ionization degree of the nitrogen atoms in systems I and II.

7 CONCLUSIONS

In the present paper the method is developed for studying the influence of the contact interaction models between the gas systems on their equilibrium compositions. This method is based on the fundamental principles of statistical physics. In this paper such a method is applied for the investigation of the multi-component plasma systems equilibrium compositions.

The relations between the equilibrium compositions of ionized gas systems I and II are derived under the different conditions of their contact interaction. In each of the situations under consideration the simplified method is used for the calculation of the basic system I equilibrium composition.

First, the conditions are considered when only thermal interaction is possible between systems I and II, and temperature T of system II is known. Then temperature of system I is also known. The method for the equilibrium composition calculation of thermally ionized gas in system I coincides with the method which is reported in Ref. [10].

Further, the situation is considered when systems I and II may exchange energy and electrons, and temperature T, and the density of free electrons in system II are known. It is shown that then not only temperatures T but also the free electrons densities coincide in systems I and II. The analytical expressions for any order ionization degree of all heavy particles in system I are obtained. It is shown that these ionization degrees do not depend on the particles densities.

At last, the case is described when systems I and II may exchange not only energy and electrons, but also heavy particles of some chemical kind. It is shown that in this case, not only temperatures T and the free electrons densities, but also the atoms and ions equilibrium densities of this chemical species coincide in systems I and II.

When in systems I and II the particles of the same chemical element are present which cannot pass through the separated surface, then the densities of these particles differ. However, their ionization degrees coincide.

The results of this study can be used for the determination of the plasma systems equilibrium compositions and ionization degrees with the application of the supplementary (experimental) inclusions.

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