ELECTRON AND ION STATISTICS IN THE THERMAL PLASMA WITH CONDENSED PHASE

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Ionization balance in the thermal plasma containing particles of the condensed disperse phase is investigated. Expressions for electron and ion distributions in plasma with an infringement of concentration balance are received. It is shown that the presence a volumetric charge in the plasma gas phase changes its ionization degree. It is offered to take the given change into account by introducing a non-equilibrium parameter whose value depends on the perturbation brought by condensed particles. The dependence of the non-equilibrium parameter on the plasma potential is determined.

Introduction

Electron and ion distributions in the low-temperature plasma are described by the classical distribution function, which is a corollary of the Fermi — Dirac statistics for a system with nondegenerate states [1]. However, in plasma with an infringement of the density equilibrium, the distributions of free and bound electrons may not be described by a single function. Nevertheless, the equilibrium equations with a single distribution function are used for the calculation of the electron and ion number densities in plasma with the condensed disperse phase whose gas phase has a volumetric charge [2 — 4]. It does not allow one to construct an adequate theoretical model of plasma with the condensed disperse phase and to explain its some specific effects, for example, long-range interactions between charged grains [5]. The indicated deficiency was noted in [6 — 8], but the statistical distributions in plasma with infringements of the density equilibrium were not studied in detail.

1. Statement of the Problem

Plasma with the condensed disperse phase is a physical analog of the plasma of combustion products (thermal smoky plasma) [5 — 8] and dusty plasma [4, 9, 10].

Dusty plasma is formed at the introduction of compact-grained dust particles in a discharge plasma and characterized by that the formation of free charges happens as a result of ionization of atoms of the gas phase due to flowing electric current at a low pressure of gas. Therefore, the plasma contains components whose kinetic energy varies strongly. Dust particles are usually submitted as polymetric compounds of the spherical or cylindrical shape and gain a charge by entrapment of electrons and ions from a gas phase, which characterizes the interaction between plasma and dust particles. This interaction in the dust plasma is usually descrobed by the orbital model [9] under assumption that an ion undergoes no collisions on the path from one dust particle (a grain) to another one. It is natural that dusty plasma can be described by the Vlasov equation.

Smoky plasma differs from dusty plasma, first of all, in that the condensed grains are formed directly in plasma as a result of the condensation of combustion products or are fuel particles that are not burnt down. Smoke grains include also the nanodispersed nuclei of grains or clusters. The condensed phase of smoky plasma is polydisperse initially, as distinct from artificial dust systems in the gas-discharge plasma where an investigator may set the dispersity of grains.

The formation of free electrons in smoky plasma happens due to thermal ionization of atoms of the gas phase or under thermionic emission from the grain surface. In plasma, the conditions for local thermodynamic equilibrium between all components of plasma are satisfied, including smoke grains, which may be both in the solid and liquid states. Since the burning is carried out at atmospheric pressure and the electron number density is sufficient for the exchange of energy by collisions, the plasma can be considered as strongly collisional. The distribution of electrostatic potential in the neighborhood of a chosen charge is described by the self-consistent Poisson — Boltzmann equation.

Smoky plasma always contains easy ionizable atoms in the gas phase, for example, a natural impurity of sodium (of the order of $10^{16} - 10^{18}$ m^{-3}). Therefore, the gas phase is noticeably ionized at temperatures 1000 — 3000 K. To increase electrical conductivity, the admixtures of the atoms of alkaline metals with the concentration up to 10^{23} m^{-3}) are introduced into plasma, and therefore the ionization of remaining atoms and molecules of gas can be neglected.

The distribution of particles in thermodynamic equilibrium gas plasmas containing single-charged positive ions, electrons, and atoms is described by the Saha equation:

$$\frac{n_{e0}n_{i0}}{n_{a0}} = 2\frac{g_i}{g_a}\left(\frac{m_e kT}{2\pi\hbar^2}\right)^{3/2} \exp\left(-\frac{I}{kT}\right) \equiv K_{\rm S}, \qquad (1)$$

where n_{e0} is the electron number density, n_{i0} is the ion number density, n_{a0} is the atom number density, g_i is the statistical weight of ions, g_a is the statistical weight of atoms, m_e is the electron mass, T is the Kelvin temperature, k is the Boltzmann constant, $\hbar$ is the Planck constant, I is the ionization potential of admixture atoms, and $K_{\rm S}$ is the Saha constant. The index 0 means that plasma contains no grains and, in any area of plasma, the condition of electroneutrality:

$$n_{e0} = n_{i0} = n_0 \qquad (2)$$

is satisfied, where n_0 is the unperturbed number density.

The interphase interaction in smoky plasma leads to a change in the amount of electrons and ions in the gas phase, because grains of the condensed phase can emit and absorb electrons and are the centers of ionization of atoms and those of recombination of ions. In this case, the mean concentrations satisfy the condition:

$$\bar{n}_i - \bar{n}_e + \bar{Z}_g n_g = 0, \qquad (3)$$

where Z_g and n_g are, respectively, is the charge number and the number density of condensed grains.

Thus, the application of the Saha equation (1) under the unbalance between electron and ion number densities in the gas phase of plasma appears impossible since it is based on expression (2) which is not true any more. Hence, the single distribution function over energies for free and bound electrons (electrons and ions) cannot be used for the description of ionization equilibrium in smoky plasma when condition (3) is satisfied. With this purpose, it is possible to apply the Shockley model similarly to how it was made in the physics of semiconductors [11] or to calculate the grand statistical sum over the states of free and bound electrons.

The present paper is devoted to the determination of the electron and ion number densities in thermal plasma with an infringement of density equilibrium in the gas phase due to the interaction with grains of the condensed phase and to methods of deriving the non-equilibrium parameter.

2. Application of the Shockley Model

In a state of thermodynamic equilibrium in the low-temperature plasma at a given temperature, there exists a certain distribution of electrons over quantum states, which yields the establishment of the equilibrium concentrations of free electrons and ions. As known, the electron states are described by the Fermi — Dirac statistics. However, if the temperature of smoky plasmas is not too high, we may use the simple Maxwell — Boltzmann distribution function. In this case, the probability to find an electron in the quantum state with energy E is defined by the expression

$$f(E,T) = \exp\frac{\tilde{\mu} - E}{kT}, \qquad (4)$$

where $\tilde{\mu}$ is the level of electrochemical potential or a Fermi level of plasma, which can be represented in our case as the sum of the chemical potential of electrons μ_e and the electron energy in an electric field:

$$\tilde{\mu} = \mu_e - e\bar{\varphi}. \qquad (5)$$

Accordingly, the electron energy is

$$E = E_0 + \frac{p_e^2}{2m_e},$$

where p_e is the electron quasimomentum and E_0 is the minimum energy of a free electron. In the unperturbed area of plasma, $E_0 = -e\bar{\varphi}$.

The average value of electrostatic potential is the sum of the potential of plasma $\varphi_{\rm pl}$ and average value of the function $\varphi(r)$, which is a solution of the Poisson — Boltzmann equation [8]:

$$\bar{\varphi} = \varphi_{\rm pl} + \langle\varphi(r)\rangle.$$

The plasma potential $\varphi_{\rm pl}$ characterizes the work, which should be performed in order that the volume of plasma gain some volumetric charge.

We obtain the electron number density from Eq. (4) by integrating over all states of the electron as

$$\bar{n}_e = \nu_e \exp\frac{\mu_e}{kT}, \qquad (6)$$

where $\nu_e = 2\left(\frac{m_e kT}{2\pi\hbar^2}\right)^{3/2}$ is the effective density of electron states.

The ion number density satisfies the relation

$$\frac{\bar{n}_i}{\bar{n}_a} = \frac{1-f}{f} = \frac{g_i}{g_a}\exp\frac{-\mu_e - I}{kT} \qquad (7)$$

which is valid only for electroneutral plasma. As was already noted, the existence of a volumetric charge does not allow one to describe electrons and ions by the single distribution function (4).

Non-equilibrium systems in the physics of semiconductors are described within the well-known Shockley model offering a formal use of different levels of electrochemical potential for different subsystems [3]. Following this model, we introduce two levels of electrochemical potential: $\tilde{\mu}$ – for the subsystem of electrons, $\tilde{\mu}^*$ – for the subsystem of ions.

Note, that $\tilde{\mu}$ it is actually the level of electrochemical potential coinciding with that in Eq. (4), whereas $\tilde{\mu}^*$ is the formal parameter showing what level of electrochemical potential could be if the electron number is equal to the actual ion number.

The difference

$$\tilde{\mu} - \tilde{\mu}^* \equiv \psi \tag{8}$$

shows the non-equilibrium nature of smoky plasmas, namely the fact that the total amount of electrons N_e is not equal to the total amount of ions N_i in the system. That is, plasma has a volumetric charge.

In fact, we suggest to use two distribution functions for free and bound electrons:

$$f(E,T) = \exp\frac{\tilde{\mu} - E}{T}$$ for the subsystem of electrons and

$$f^*(E,T) = \exp\frac{\tilde{\mu}^* - E^*}{T}$$ for the subsystem of ions.

The presence of the volumetric charge means the existence of some average value of potential which defines the minimum value of the energy spectrum of free electrons, $E_0 = -e\bar{\varphi}$. In this case, Eqs. (5) and (6) remain to be valid for the subsystem of electrons.

For the subsystem of ions, the formal value $\tilde{\mu}^*$ corresponds to the quasineutral state of plasma for a given value of the ion number density n_i. Hence, $E_0^* = -e\bar{\varphi}^* = 0$, and the chemical potential of electrons $\mu_e^* = \tilde{\mu}^*$. Then the ion number density can be presented as

$$\bar{n}_i = \bar{n}_e^* = \nu_e \exp\frac{\mu_e^*}{kT}.$$

In the non-equilibrium plasma, it is necessary to use the following expression for the ion number density instead of (7):

$$\frac{\bar{n}_i}{\bar{n}_a} = \frac{1 - f^*}{f^*} = \frac{g_i}{g_a}\exp\frac{E_0 - I - \tilde{\mu}^*}{kT} =$$

$$= \frac{g_i}{g_a}\exp\frac{-\mu_e - I + \psi}{kT}. \tag{9}$$

Thus, the use of the Shockley model allows us to extend the relations of statistics on non-equilibrium states of plasma. Really, if the volumetric charge is absent and $N_e = N_i$, then the non-equilibrium parameter ψ=0 and relation (9) passes to (7).

By multiplying the number densities of electrons (6) and ions (7), we obtain the well-known Saha equation (1) for electroneutral plasma. Under the presence of a volumetric charge of plasma, it is necessary to use (9) for the ion number density, whence we obtain the relation:

$$\frac{\overline{n_e n_i}}{\overline{n_a}} = \frac{g_i}{g_a}\nu_e \exp\frac{-I + \psi}{kT} = K_S \exp\frac{\psi}{kT}. \tag{10}$$

Thus, relation (10) allows us to determine the quasi-equilibrium number densities of charges by introducing the effective potential of ionization depending on the non-equilibrium parameter ψ.

3. Application of the Statistical Sums

The non-equilibrium parameter ψ is, in fact, the correction to the ionization potential in (10) and can be determined by the calculation of statistical sums. For this purpose, we will find the average value of the electrostatic potential affecting an electron and take the electrostatic energy into account in the grand statistical sum.

Under the presence of charged grains in plasma, there exist some average value of the potential [8]:

$$\bar{\varphi} = \varphi_{pl} + \langle\varphi\rangle, \quad \langle\varphi\rangle = \frac{1}{V}\int_V \varphi(\mathbf{r})dV. \tag{11}$$

Let us write the grand statistical sum for the subsystem of free electrons:

$$Z = \sum_{N_e}\sum_i \exp\left[\frac{\tilde{\mu}N_e - E_i(N_e) + e\bar{\varphi}N_e}{kT}\right]. \tag{12}$$

For the electron number density, formula (12) yields [12]:

$$\tilde{\mu} + e\bar{\varphi} = kT\ln\frac{\bar{n}_e}{\nu_e}. \tag{13}$$

At the same time, the plasma contains some number of ions N_i, which is not equal to the number of electrons N_e. But we suppose that some number of electrons N_e^* is equal to the real number of ions: $N_e^* = N_i$. Then the plasma becomes electroneutral, and the grand statistical sum reads

$$Z^* = \sum_{N_e^*} \sum_i \exp\left[\frac{\tilde{\mu}^* N_e^* - E_i(N_e^*)}{kT}\right]. \tag{14}$$

This relation yields

$$\tilde{\mu}^* = kT \ln \frac{\bar{n}_e^*}{\nu_e} = kT \ln \frac{\bar{n}_i}{\nu_e}. \tag{15}$$

We define a non-equilibrium parameter as the difference of the real value of electrochemical potential and its formal value,

$$\psi \equiv \tilde{\mu} - \tilde{\mu}^* = -e\varphi_{\rm pl} - e\langle\varphi\rangle + kT \ln \frac{\bar{n}_e}{\bar{n}_i}. \tag{16}$$

In view of the condition $e\langle\varphi\rangle << kT$ which is usually valid in thermal plasma [8], we arrive at the relation

$$\frac{\bar{n}_e}{\bar{n}_i} = 1 + 2\frac{e\langle\varphi\rangle}{kT}.$$

Then expression (16) can be represented as

$$\psi = -e\varphi_{\rm pl} + e\langle\varphi\rangle \cong -e\varphi_{\rm pl}. \tag{17}$$

It is clear that the non-equilibrium parameter is defined by a value of the plasma potential which characterizes the electrostatic energy of the gas phase of smoky plasma.

4. The Non-Equilibrium Parameter

We now determine the dependence of the concentrations of components of the gas phase of plasma on the non-equilibrium parameter. For this purpose, we express the ion number density by the own chemical potential μ_i [12, 13]:

$$\bar{n}_i = g_i \left(\frac{m_i kT}{2\pi\hbar^2}\right)^{3/2} \exp\frac{\mu_i}{kT} = \nu_i \exp\frac{\mu_i}{kT}. \tag{18}$$

Further, relations (9) and (18) yield

$$\mu_i = kT \ln \frac{\bar{n}_a}{g_a\left(\frac{m_i kT}{2\pi\hbar^2}\right)^{3/2}} - \mu_e - I + \psi.$$

Then, taking into account that $m_i \approx m_a$ and the chemical potential of atoms is

$$\mu_a = kT \ln \frac{\bar{n}_a}{g_a\left(\frac{m_a kT}{2\pi\hbar^2}\right)^{3/2}} - I,$$

we obtain the relation

$$\mu_e + \mu_i - \mu_a = \psi. \tag{19}$$

We note that relation (19) was obtained for the first time for plasma with a condensed phase in [7] as a result of the variation of the free energy of the system as a whole, by assuming the functional interrelation between the density of free electrons and the number density of grains with some charge on the surface. The analysis of expression (19) allows us to conclude that a value of the parameter ψ can be characterized as a change of the free energy of the gas phase subsystem due to the interphase interaction of the gas with grains.

Interphase interaction is meant as the transport of an electron through the interface, which can occur directly or through the ionization of an atom or the recombination of an ion on the grain surface. The chemical potential of each component of the gas subsystem can change its value according to a change in the density. Then it is possible to define the non-equilibrium parameter of each component. It is obvious that the sum of the non-equilibrium parameters of components is equal to the parameter ψ. As follows from expression (17), the potential of electroneutral plasma and its average value are equal to zero. Therefore, the parameter ψ is equal to zero as well, and expression (19) passes to the known equation characterizing the chemical equilibrium in gas plasma: $\mu_{e0} + \mu_{i0} - \mu_{a0} = 0$.

To determine the chemical potential of components of the gas phase, we shall take their values in electroneutral plasma as initial ones:

$$\mu_e = \mu_{e0} + \psi_e, \quad \mu_{e0} = kT \ln \frac{n_0}{\nu_e};$$

$$\mu_i = \mu_{i0} + \psi_i, \quad \mu_{i0} = kT \ln \frac{n_0}{\nu_i};$$

$$\mu_a = \mu_{a0} - \psi_a, \quad \mu_{a0} = kT \ln \frac{n_{a0}}{\nu_a} - I. \tag{20}$$

In this case, we get $\psi_e + \psi_i + \psi_a = \psi$, $n_{a0} = N_a - n_0$.

The presence of a volumetric charge in plasma leads to a displacement of ionization equilibrium and, accordingly, to a change in the concentrations of plasma components:

$$\bar{n}_e = n_0 + \delta n_e = n_0 \exp\frac{\psi_e}{kT},$$

$$\bar{n}_i = n_0 + \delta n_i = n_0 \exp\frac{\psi_i}{kT},$$

$$\bar{n}_a = n_{a0} - \delta n_a = n_{a0} \exp \frac{-\psi_a}{kT}. \quad (21)$$

These relations yield that $\psi_e - \psi_i = 2e\langle\varphi\rangle$. By using this relation and (17) and setting $\psi_e, \psi_i >> \psi_a$, we obtain the following formulas for the electronic and the ionic components of the non-equilibrium parameter:

$$\psi_e = -{}^1\!/_2 e\varphi_{\rm pl} + 1{}^1\!/_2 e\langle\varphi\rangle, \quad \psi_i = -{}^1\!/_2 e\varphi_{\rm pl} - {}^1\!/_2 e\langle\varphi\rangle. \quad (22)$$

Relations (22) mean that, at the presence of charged particles in plasma, the average electron and ion concentrations differ a little, $\bar{n}_e \approx \bar{n}_i$, because $e\langle\varphi\rangle << e\varphi_{\rm pl}$, but they can strongly differ from n_0. This implies that plasma compensates the perturbations introduced by grains by a change in the ionization degree.

It is necessary to consider the potential distribution in the form $\varphi_{\rm pl} + \varphi(\mathbf{r})$ near grains of the condensed phase or on the plasma volume boundary, where there are considerable potential barriers. Then the relations for electron and ion concentrations are transduced to the usual Boltzmann distribution:

$$n_e(\mathbf{r}) = n_q \exp \frac{e\varphi(\mathbf{r})}{kT}; \quad n_i(\mathbf{r}) = n_q \exp \frac{-e\varphi(\mathbf{r})}{kT}, \quad (23)$$

where the quasi-nonperturbed concentration n_q is determined from (21) and (22) as

$$n_q = \sqrt{\bar{n}_e \bar{n}_i} = n_0 \exp \frac{\psi}{2kT} \quad (24)$$

and is a function of the plasma potential, because the non-equilibrium parameter ψ is linearly connected to it.

Conclusion

In thermal plasma with a condensed phase (smoky plasma), the ionization degree depends on the volumetric charge of the gas phase. A value of the volumetric charge $Q_{\rm pl}$ defines a value of the plasma potential, which can be obtained from the energy of an electric field with intensity E:

$$\varphi_{\rm pl} Q_{\rm pl} = \varepsilon_0 \int_V E^2 dV, \quad Q_{\rm pl} = eN_i - eN_e.$$

The plasma potential is directly connected to the non-equilibrium parameter $\psi \cong -e\varphi_{\rm pl}$. Therefore, the ionization equilibrium in smoky plasma can be described by using the modernized Saha equation as

$$\frac{\overline{n_e n_i}}{\overline{n_a}} = K_{\rm S} \exp \frac{-e\varphi_{\rm pl}}{kT}.$$

The perturbations introduced to plasma by grains of the condensed phase lead to a displacement of the ionization equilibrium of the gas phase and a change in the electron and ion concentrations. Though we have considered only the perturbations represented as a change in the gas phase charge, the offered procedure is suitable for other kinds of perturbations creating the additional channels of ionization and recombination. On the other hand, collisions between gas particles are the sole channel of ionization in thermal gas plasma. Namely this process is described by the Saha equation. Any external action on the plasma giving rise to a change in the ionization and recombination processes to one or other side induces a displacement of the ionization equilibrium and can be described within the model developed in the present paper.

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СТАТИСТИКА ЕЛЕКТРОНІВ І ІОНІВ У ТЕРМІЧНІЙ ПЛАЗМІ З КОНДЕНСОВАНОЮ ФАЗОЮ

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Р е з ю м е

Досліджено іонізаційну рівновагу у термічній плазмі, що містить частинки конденсованої дисперсної фази. Отримано вирази для розподілу електронів і іонів у плазмі з порушенням концентраційної рівноваги. Показано, що наявність у газовій фазі плазми об'ємного заряду приводить до зміни ступеня її іонізації. Запропоновано враховувати ці зміни шляхом введення параметра нерівноважності, значення якого залежить від збурення, що його вносять частинки конденсованої фази. Визначено залежність параметра нерівноважності від потенціалу плазми.