Thermodynamics of complex plasmas with two different sorts of macroions

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Abstract. Three-component electroneutral systems of finite-size classical macroions with two different charge numbers $Z_1 \gg 1$ and $Z_2 \gg 1$ and point-like oppositely charged microions are analyzed. Free energy of a mixture of two sorts of macroions is estimated within the Wigner–Seitz cells approximation. The non-linear screening effect is taken into account via the Poisson–Boltzmann approximation within the both cells. The equality of microions pressures at the boundary between the co-existing cells with the different sorts of macroions is used as an equilibrium condition. The difference between the total Helmholtz free energy in equilibrium is shown in comparison with the situation when the Wigner–Seitz cells with macroions with the different charges have the same volumes.

1. Introduction

Multi-component complex plasmas are well-represented in nature and laboratory experiments. The complex plasma consists of microions and macroions which are usually much bigger than the former. Both microions and macroions have electric charges and the complex plasma is electroneutral. In general case, systems with many sorts of macroions are of great interest because they are widely spread in nature (dust in microprocessors, moon dust, noctilucent clouds and even laboratory plasmas) [1].

One of the phenomena of the complex plasma with many sorts of macroions and microions is a non-congruence of phase transitions. A non-congruent phase transition is the most common form of first-order phase transitions in equilibrium systems which consist of two or more chemical elements, e.g., in mixtures or compounds [2,3]. One of distinctive properties of the non-congruent phase transitions is the fact that all the interphase boundaries in intensive thermodynamic variables, e.g., $P(T)$, must be not a curve like in the van der Waals transition gas–liquid or in a melting, but a zone for a non-congruent transition. The key condition to realize a non-congruent situation in the complex plasma is an existence of two or more sorts of charged particles. However, if the system is electroneutral then there should be at least three different charged sorts of particles (see, e.g., [4]).

The important problem for studying of the non-congruent phase transitions is describing thermodynamics of the system, especially total Helmholtz free energy. In this paper, we employ the Wigner–Seitz approximation to consider the system which consists of two different sorts of...
macroions. Additionally, we take non-linear screening of the macroions by the microions into account. The Poisson–Boltzmann equation is as follows:

$$\Delta \varphi(r) = -4\pi n_{i0} e \exp \left( -\frac{e \varphi(r)}{kT} \right),$$

(1)

where $\varphi(r)$ is the average electrostatic potential, which is created by the central macroion and the surrounding microions; $n_{i0}$ is microions concentration at the border of an average electroneutral spherically-symmetric cell. The Poisson–Boltzmann equation is usually solved not in cells only. For example, Bystrenko and Zagorodny [5] solved it numerically for a test macroion in the infinite electroneutral two-component plasma of positively and negatively charged microions. For example, Bystrenko and Zagorodny [5] solved it numerically for a test macroion in the infinite electroneutral two-component plasma of positively and negatively charged microions. D’yachkov [6] solved this equation analytically for the same problem as in [5]. We compared some our results with theirs in [7] where we described how we used the Poisson–Boltzmann approximation in the spherically-symmetrical cell. Moreover, Tsyтовich and Gusein-zade [8] considered both situations of linear and non-linear screening, however, their review dealt with describing kinetics and non-linear scattering of ions from dust grains. In addition, Zhukhovitksiy et al [9] considered some analytical extreme events for the Wigner–Seitz cell and a test macroion in an infinite plasma of positive microions and electrons.

In the context of our future interest of considering multi-component systems, we take into account the exponent in the Poisson–Boltzmann equation and calculate the potential different from the Yukawa one. Moreover, the Yukawa potential is not adequate for describing the real complex plasma. It is so because the linearization condition $|e \varphi(r)/(kT)| \ll 1$ is valid only for a small part of typical values of the systems which are considered in this paper. Prototypes of these systems include idealized models of a dusty plasma of gas discharges [1], a colloidal plasma (see, e.g., [10]), a plasma with condensed dispersed phase (CDP plasma) [9], and a dusty plasma of noctilucent clouds [11]. The typical values of dusty plasmas of gas discharges are the following: macroions charge number $Z \sim 10^3$–$10^4$, macroions concentration $n_Z \sim 10^3$–$10^4$ cm$^{-3}$, macroions temperature $T_Z \approx 1$–2 eV, microions temperature $T_i \approx 0.03$ eV. The typical values of CDP plasma are $n_Z \sim 10^8$–$10^{14}$ cm$^{-3}$, $T_i \approx 2000$–3000 K. The typical values of colloidal plasma are room temperature and $Z \sim 10$–$10^3$. The typical values of dusty plasmas in noctilucent clouds are the following: maximum $Z \sim 10^2$, $T_Z = T_i \approx 0.03$ eV. Therefore, as $T_i = 0.03$ eV and $R_Z = 1$ μm, the inequality $Ze^2/(R_Z T) \leq 1$ is correct since $Z \leq 22$. Hence, the linearization condition can be used chiefly for not too big values of macroions charges.

In section 2, we explain how we obtain the total Helmholtz free energy of the mixture of the Wigner–Seitz cells with the central macroions of both sorts. Section 3 presents conclusions.

2. Total Helmholtz free energy of the system with two sorts of macroions and one sort of microions

In this paper, we employ the Wigner–Seitz approximation to consider the system which consists of two sorts of macroions having the same radii $R_Z$ and different charges. For definiteness, we consider macroions with charges $-Z_1 e$ and $-Z_2 e$ (hereafter $Z_1$ and $Z_2$ will be referred to as “charges”), $Z_1 \gg 1$ and $Z_2 \gg 1$, and one sort of microions with the charge $e$. Thus, we consider electroneutral Wigner–Seitz cells with the central macroions of two sorts (with the charges $Z_1$ and $Z_2$) and the microions surrounding the macroions. The temperature $T$ of both macroions and microions is the same.

At first, the cells of both types are placed in an imaginary box with a constant volume at the ratio $\alpha : (1 - \alpha)$, where $\alpha = N_1/(N_1 + N_2)$ is the portion of the constant number of macroions of the first sort $N_1$ in comparison to the constant number of macroions of both sorts $N_1 + N_2$. Initially, all the cells have the same volume $V_0$. Then the cells mix. The cells of one type begin getting smaller and the cells of another type expand in order to get to the equilibrium. This is due to the fact that pressures of all the cells should be equal in equilibrium. The pressure
equality leads to the equality of the microions concentrations at the borders of all co-existing cells (this will be evident later after writing the equation of the total Helmholtz free energy of each cell). Because of the electroneutrality of each cell, the cells with the smaller macroion charges (for example, with $Z_1$) will begin getting smaller and the cells with another macroion charge (with $Z_2$) will expand.

In this section, we would like to show how the total Helmholtz free energy changes under conditions of thermodynamic stability compared with the situation when all cells have the same volumes.

The total Helmholtz free energy is $F_{\text{tot}} = \alpha F_1 + (1 - \alpha) F_2$, where $F_1$ and $F_2$ are the total Helmholtz free energies of the cells with the macroions of the first and the second sorts respectively (hereafter we will refer to these cells as the cells of the first and the second types respectively). It is evident that as there is one macroion in each cell only, the value $N_1$ is also the number of the cells with the macroions with the charge $Z_1$, while $N_2$ is the number of the cells with the macroions with the charge $Z_2$. The dimensionless Helmholtz free energy is $f_{\text{tot}} = F_{\text{tot}}/((N_1 + N_2) kT)$. It is well-known (see, e.g., [12]) that

$$f_{\text{tot}} = \alpha (u_{\text{ex}1} + f_{i1}) + (1 - \alpha) (u_{\text{ex}2} + f_{i2}),$$

(2)

where $u_{\text{ex}1}$ and $u_{\text{ex}2}$ are the dimensionless Coulomb interaction energies (non-ideal portions of internal energies), $u_{\text{ex}j} = U_{\text{ex}j}/(N_j kT)$, $j$ is a sort of the cell, $U_{\text{ex}j}$ is the Coulomb interaction energy of the $j$-th type cell, and $f_{i1}$ and $f_{i2}$ are the dimensionless free energies of microions ideal gas in the cells of the first and the second types, $f_{ij} = F_{ij}/(N_j kT)$, $F_{ij}$ is the free energy of microions ideal gas of the $j$-th type cell. The interaction energy of each cell consists of macro–micro interaction energy and micro–micro interaction energy. The macro–micro interaction energy of the cell of the first type is

$$u_{Zi1} = \frac{Z_1 e}{kT} \left( \varphi_{Zi1}(r) - \frac{Z_1 e}{r} \right) \bigg|_{r \to R_z},$$

(3)

where $\varphi_{Zi1}(r)$ is the average electrostatic potential which is created by the macroion and the microions in the cell of the first type, $(\varphi_1(r) - Z_1 e/r) \big|_{r \to R_z}$ is the potential which is created by all microions inside the cell of the first type on the surface of the central macroion. The micro–micro interaction energy of the first type cell is

$$u_{i1} = \frac{1}{2} \int_{R_z}^{R_1} \left( \frac{e \varphi_{Zi1}(r)}{kT} - \frac{Z_1 e^2}{r kT} \right) 4\pi r^2 n_{i1}(r) \, dr,$$

(4)

where $R_1$ is the radius of the first type macroions in equilibrium, $n_{i1}(r)$ is a distribution of microions concentration in the first type cell. Therefore, the total interaction energy of the first type cell is

$$u_{\text{ex}1} = \frac{Z_1 e}{kT} \left( \varphi_{Zi1}(r) - \frac{Z_1 e}{r} \right) \bigg|_{r \to R_z} + \frac{1}{2} \int_{R_z}^{R_1} \left( \frac{e \varphi_{Zi1}(r)}{kT} - \frac{Z_1 e^2}{r kT} \right) 4\pi r^2 n_{i1}(r) \, dr.$$  

(5)

The dimensionless microions ideal-gas free energy in the first type cell is

$$f_{i1} = \int_{R_z}^{R_1} 4\pi r^2 n_{i1}(r) \left( \ln(n_{i1}(r)) \right) - 1) \, dr,$$

(6)

where $\lambda_1 = \hbar/(2\pi m_i kT)^{1/2}$ is the Broglie wavelength, $m_i$ is the mass of the microion (neon or argon are usually used in, e.g., dusty plasmas of gas discharges). Now it is easy to prove that as pressure of a cell is $P_{\text{ex}j} = -\langle \partial (u_{\text{ex}j} + f_{ij})/\partial V_{\text{cell}j} \rangle_r$, where $V_{\text{cell}j}$ is a cell volume that changes to get to the equilibrium, thus, $n_{i1}(R_1) = n_{i2}(R_2)$, where $n_{i1}(R_1)$ and $n_{i2}(R_2)$ are microions concentrations at the borders of the first type cells and second type cells in equilibrium respectively, $R_2$ is the radius of the second type macroion in equilibrium.
Figure 1. The dimensionless energies as a function of $\alpha$ (the portion of the cells number with the macroion having the charge $Z_1$ to the total number of the macroions). Macroions radii are $R_Z = 1$ $\mu$m, temperature is $kT = 0.03$ eV, $Z_1 = 500$, $Z_2 = 100$, the initial volume of all the cells (when there is an imaginary partition between the cells of the different types) is $V_0 = 10^{-8}$ cm$^3$. Line 1 corresponds to the total constant portion of the total microions free energy $f_{\text{const}}$ [(9) and (10)]; line 2 corresponds to the total Helmholtz free energy $f_{\text{tot}}$ (2); line 3 corresponds to the total Coulomb interaction energy $u_{\text{ex}}$, while line 4 corresponds to the rest portion of the total microions free energy (11).

As the cells are electroneutral, we have

$$\int_{R_Z}^{R_1} 4\pi r^2 n_{i1}(r) \, dr = Z_1,$$

for the first type cell, and it means that

$$f_{i11} = \int_{R_Z}^{R_1} 4\pi r^2 n_{i1}(r) \ln(n_{i1}(r)) \, dr + f_{\text{const1}},$$

where

$$f_{\text{const1}} = Z_1(\ln(\lambda_i^2) - 1)$$

is a constant. All the equations (3)–(9) are valid for the second type cell if we change subscript 1 to 2. Therefore, total constant portion of microions ideal-gas free energy is

$$f_{\text{const}} = \alpha f_{\text{const1}} + (1 - \alpha) f_{\text{const2}}.$$  

Figure 1 shows the total constant fraction of the total free energy of microions $f_{\text{const}}$, the total Helmholtz free energy $f_{\text{tot}}$, the total Coulomb interaction energy $u_{\text{ex}} = \alpha u_{\text{ex1}} + (1 - \alpha) u_{\text{ex2}}$; the rest portion of the total microions free energy

$$f_{\text{var}} = \alpha f_{i11} + (1 - \alpha) f_{i12} - f_{\text{const}}.$$  

It is naturally to assume that line 2 should be concave because the total Helmholtz free energy absolute value approaches to increase in equilibrium [12] in comparison to non-equilibrium states.
Figure 2. The absolute value of the difference between the total Helmholtz free energy $f_{\text{tot}}$ in equilibrium and $f_{V0}$ in the case when all the cells have the same volume $V_0$ (macroions radii $R_Z = 1 \ \mu m$, temperature $kT = 0.03 \ \text{eV}$, macroions charges $Z_1 = 500$ and $Z_2 = 100$). Line 1 corresponds to the initial cells volume $V_0 = 10^{-8} \ \text{cm}^3$, while line 2 corresponds to $V_0 = 10^{-6} \ \text{cm}^3$.

However, the increase is much smaller than the value of total Helmholtz free energy $f_{\text{tot}}$. We show this increase in figure 2, where $\Delta f = f_{\text{tot}} - f_{V0}$, $f_{V0}$ is total Helmholtz free energy of the system when all the cells have the volume $V_0$.

We can use the linear mixing rule for systems with three, four and more sorts of the macroions. Therefore, we should write

$$f_{\text{total}} = \sum_j \alpha_j (u_{exj} + f_{iij}),$$

where $f_{\text{total}}$ is the total Helmholtz free energy of the system with $j$ sorts of the macroions, $\alpha_j$ is the portion of the $j$-th type cells number (with the macroion having the charge $Z_j$) to the total number of the macroions, $u_{exj}$ and $f_{iij}$ are the dimensionless Coulomb interaction energy and the dimensionless free energy of microions in the cells of the $j$-th type. Equations (3)–(9) can be rewritten to the $j$-th type cell if we change subscript 1 to $j$.

3. Conclusions
The total Helmholtz free energy of isochoric mixing was calculated via the Poisson–Boltzmann approximation in frames of the mixed Wigner–Seitz cells model. The non-linear screening of the macroions by the microions was taken into account. The boundary microions pressure equality was used as an equilibrium condition. The presented procedure to obtain the total Helmholtz free energy can be used for systems with any number of the macroions sorts.

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