Effect of non-linear screening on thermodynamic properties of complex plasma

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Abstract. This work is devoted to the analysis of the applicability range of a basic assumption in the phase diagram of complex plasma, i.e., linearized (Debye) screening of macroions by microions, which leads to the Yukawa form of effective interactions between macroions. Parameters of non-linear screening for macroions were calculated within the direct Poisson–Boltzmann approximation. Two effects were revealed as a result of such calculations: (i) decomposition of all microions into two subclasses, free and bound ones, and (ii) significant reduction of an effective charge $Z^*$ of the initial bare macroion $Z$ under non-linear screening by a small high-density envelope of the bound microions. The effective charge $Z^*$ grows in the direct proportion to $Z$ first and then, the change of $Z^*$ is negligibly thin. This renormalization of the initial $Z$ and macroion concentration at the border of the cell leads to corresponding renormalization of initial $\Gamma$ and $\kappa$ into $\Gamma^*$ and $\kappa^*$ ($\Gamma^* < \Gamma$ and $\kappa^* < \kappa$). The corresponding calculated shifts of excess internal energy are discussed and illustrated.

1. Introduction

Non-linear screening is a really important effect when describing thermodynamics of complex plasma. Failure to take this effect into account leads to incorrect thermodynamic functions and thermodynamic instability. In the present paper we consider two-component equilibrium electroneutral systems which consist of macroions with an absolute value of the charge number $Z$ ($Z \gg 1$), concentration $n_Z$, temperature $T_Z$ and radius $R_Z$ and one sort of point-like opposite charged microions with the charge number 1, density $n_i$ and temperature $T_i$. The phase diagram of complex plasmas is obtained in [1]. There are three phase states: fluid, bcc (base-centered cubic lattice) crystal and fcc (face-centered cubic lattice) crystal. The phase diagram [1] is plotted in the $\kappa$–$\Gamma$ plane

$$\kappa = \frac{a}{r_D}, \quad \Gamma = \frac{(Ze)^2}{kT_Z} \left(\frac{4\pi n_Z}{3}\right)^{1/3},$$

(1)

where $\kappa$ is a structural parameter, $\Gamma$ is a coupling parameter, $a = [3/(4\pi n_Z)]^{1/3}$ is the Wigner–Seitz radius, $r_D = [4\pi e^2(n_i)/(kT_i)]^{-1/2}$ is the Debye radius, $\langle n_i \rangle$ is positive microion averaged concentration.
The effective macroion pair-interaction potential has the Yukawa form [1]:

$$\varphi_{Yu}(r) = \frac{Ze}{r} \exp\left(-\frac{r}{r_D}\right).$$

(2)

However, though the phase diagram was obtained for one-component system, Hamaguchi and Farouki considered and obtained thermodynamics for many-component systems (see [2, 3] for details). A description of thermodynamics of one-component dusty plasma can be found, for example, in [4].

We consider simplified two-component models of the following systems: dusty plasma of gas discharges, colloidal plasma, thermal plasma with condensed dispersed phase (CDP plasma) and dusty plasma in noctilucent clouds. Representative quantities of the mentioned systems are the following: $\Gamma \sim 10^2$–$10^5$, $\kappa \approx 0$–$10$, $Z \sim 10^3$–$10^4$, $n_Z \sim 10^3$–$10^4$ cm$^{-3}$, $T_Z \approx 1$–$2$ eV, $T_i \approx 0.03$ eV for dusty plasma of gas discharges [5]; $\Gamma \sim 10$–$10^3$, $\kappa \approx 0$–$10$, $Z \sim 10$–$10^3$, $n_Z \sim 10^3$–$10^{14}$ cm$^{-3}$, $T_i \approx 2000$–$3000$ K for CDP plasma [7]; $\Gamma \sim 1$, $\kappa \approx 0$–$10$, maximum $Z \sim 10^2$, $T_Z = T_i \approx 2.03$ eV for dusty plasma in noctilucent clouds [8]. Henceforward, we will consider systems with equal temperatures $T_Z = T_i = T$.

It was stressed previously [9] that huge regions of negative total pressure and negative total compressibility exist in the phase diagram [1] as non-ideal corrections $P_{ex}(T_Z, T_i, Z, n_Z)$ from [1] and [10] in total equations of state of complex plasma are used:

$$P_{\text{fluid}} = n_Z kT + n_i kT + P_{ex}.$$  

(3)

There should be a phase separation in an equilibrium system as the negative total compressibility means that the state of the system is not uniform. It should lead to a decomposition to phases of different densities like in [11] where highly asymmetric Coulomb systems which consist of finite sized macroions and point-like microions were considered using Monte-Carlo free energy calculations. This decomposition is absent in the initial phase diagram [1].

We stress that the phase diagram [1] is not valid for real complex plasma. The non-ideality corrections [1–3, 10] are written for a Debye system. A phase separation (a phase transition of gas–crystal and (or) even gas–liquid type because of attraction of macro- and microions) should be expected there. However, these equations of state [1–3, 10] were obtained without taking the non-linear screening effect into account.

It was shown in [12] that non-linear screening effect stabilizes charged colloidal suspensions against fluid–fluid phase separation. It means that this effect makes the phase transition at least weaker. Thus, we expect that areas of negative total pressure and negative total compressibility will be at least smaller in [12] if this effect would be taken into account.

One should solve the Poisson–Boltzmann equation with the use of the linearization condition $|e\varphi(r)/(kT_i)| \ll 1$, where $\varphi(r)$ is average electrostatic potential, to get the potential of the Yukawa form like in [13]. However, in the present paper as $T_i = 0.03$ eV and $R_Z = 1$ $\mu$m, $Ze^2/(R_Z kT_i) \leq 1$ is valid as $Z \leq 22$. So, the linearization condition should not be used because the representative charge of complex plasmas is usually much greater than 22 (see [9, 14] for details). Thus, the potential of the Yukawa form is not adequate to describe thermodynamics of considered systems. This inadequacy was also demonstrated in [15]. It means that one of significant limitations in the phase diagram [1] is neglect of the non-linear screening effect.

The paper is organized as follows. In section 2 we propose a renormalization of the initial bare macroion charge due to the non-linear screening effect and show how the effective value of charge $Z^*$ depends on $Z$. In section 3 we demonstrate that excess internal energy which obtained using the Poisson–Boltzmann equation without the linearization condition differs significantly from the ones defined in [1, 3, 10] where exponential factors in microions distributions were linearized. Section 4 presents conclusions.
Figure 1. Total charge in the sphere with the radius $r$ ($Z = 25$, $\Gamma_{ii} = 0.1$, $\chi = 20$). Red dashed line is obtained in [16]. We obtained black solid line.

2. Renormalization of the bare macroion charge $Z$

We solved the Poisson–Boltzmann equation

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

(4)

where $n_{i0}$ is microions concentration at the border of an electroneutral spherically-symmetric cell with a central macroion with negative charge $-Z$ and radius $R_Z$ and point-like microions with charge number $+1$. The radius of the cell is $R$ and $(4/3)\pi R^3 n_Z = 1$. We compared the resulting potential and the absolute value of a total charge $q$ in the sphere with the radius $r > R_Z$ with those from [16] and [17] ($q(r) = Z - Z_{\text{micro}}(r)$, where $Z_{\text{micro}}(r)$ is the absolute value of microions charge in the sphere with the radius $r$) and they practically coincide (see [14] and figure 1 for details). We used the following parameters

$$\Gamma_{ii} = \frac{e^2}{kT_i} (4\pi n_i)^{1/3}, \quad \chi = \frac{Ze^2}{kT_i R_Z}.$$  

(5)

The difference in the right part in figure 1 is easy to explain. Bystrenko and Zagorodny [16] considered a sample macroion in infinite electroneutral plasma which consists of two sorts of microions while we considered an electroneutral cell with the macroion in its center. Also, the Poisson–Boltzmann equation with a sample macroion in infinite electroneutral plasma of positive microions and electrons was solved in [15]. Besides, Tsytovich and Gusein-zade [15] also considered kinetics of dusty plasma and non-linear scattering of ions from dust grains. We remind that we consider equilibrium systems without any ion and electron fluxes.

We separated microions into two types: bound and free. This procedure is well-known (see, for example, [12]). The macroion charge $Z$ seems to be smaller at averaged distances between macroions in real complex plasma because of the bound microions. As a result, the screening is performed by the free microions. In such a way, $Z^*$ is determined as a total value of free microions

$$Z^* = \frac{4\pi}{3} n_{i0} (R^3 - R_Z^3).$$

(6)
Figure 2. Effective charge $Z^*$ as a function of a real one $Z$. Dashed lines are from [12]. Solid lines are obtained by us ($R_Z = 5.9 \, \mu m$ for blue lines 1a, 2a and 4, $R_Z = 1 \, \mu m$ for red lines 5 and 6). Lines 1a, 1b and 5 are obtained for $\phi = 5 \times 10^{-8}$, lines 2a, 2b and 6 are for $\phi = 5 \times 10^{-6}$, line 3 is for $\phi = 5 \times 10^{-1}$, line 4 is for $\phi = 5 \times 10^{-4}$.

Then $\kappa$ and $\Gamma$ also should be renormalized. Effective parameters are

$$\Gamma^* = \frac{(Z^* e)^2}{kT_Z} \left( \frac{4\pi n_Z}{3} \right)^{1/3}, \quad \kappa^* = \left( \frac{3}{4\pi n_Z} \right)^{1/3} \left( \frac{4\pi e^2 n_{i0}}{kT_i} \right)^{-1/2}.$$  \hspace{1cm} (7)

It is obvious that $\Gamma^* < \Gamma$ and $\kappa^* < \kappa$ since $Z < Z^*$ and $n_{i0} < \langle n_i \rangle$ [18]. Nefedov et al [19] also showed that an effective coupling parameter is smaller than a real one. However, they defined the effective parameter differently $\Gamma^*_{\text{Nef}} = R_Z^2 \varphi_{\text{eff}}^2 / (r_{i\text{int}} T) \exp(-r_{i\text{int}} / r_D)$, where $r_{i\text{int}}$ is interparticle distance, $\varphi_{\text{eff}}$ is macroion surface effective potential which seems to be smaller than a real one at averaged distances.

We suppose that the phase state of a system of macroions and microions is defined by an effective interaction at averaged distances when it is assumed to be of the Debye type with the effective charge $Z^*$, macroions are screened by the free microions only and the Debye radius is $r_D^* = \left[4\pi e^2 n_{i0} / (kT_i)\right]^{-1/2}$. Thus, we make an assumption that a real phase state corresponds to a phase state in the initial phase diagram but in $\kappa^* - \Gamma^*$ plane instead of the $\kappa - \Gamma$ one.

Diehl et al [12] also considered macroions with finite sizes and point-like microions so that the whole system (polyelectrolyte) was electroneutral. Due to the strong electrostatic interaction between the macroions and the microions, they expected that the asymmetric polyelectrolyte would be composed of clusters consisting of one macroion and $1 \ll n_i < Z$ associated microions. So, Diehl et al [12] also separated microions into two types. However, they did not solve the Poisson–Boltzmann equation. They obtained microion–macroion contribution using the Debye–Hückel–Bjerrum (DHB) theory. They used an extension of the DHB theory to the fluid state of a highly asymmetric colloid which was considered in [20]. Tamashiro et al [20] proved that though the linearization was not valid, however, since the formation of clusters was taken into account, the validity of the theory was extended into the non-linear regime. So, Diehl et al [12] replaced $Z$ to $Z^*$ in all formulas and defined the effective charge as $Z^* = Z - Z_b$, where $Z_b$ is an absolute value of bound microions charge. We compared their and our $Z^*$ dependences on $Z$ for different $\phi = (4\pi / 3) n_Z R_Z^3$ (figure 2). The effective charge $Z^*$ grows in the direct proportion dependence.
Figure 3. The dimensionless potential at the border of the macroion as a function of $Z$. Dashed lines are tangents $Ze^2/(R_Z kT_i)$. Red solid lines 1 and 3 and red dashed line 6 are obtained for $R_Z = 1 \mu$m, blue solid lines 2, 4 and 5 and blue dashed line 7 are obtained for $R_Z = 5.9 \mu$m. Parameter $\phi = 5 \times 10^{-8}$ for lines 1 and 2, $\phi = 5 \times 10^{-6}$ for lines 3 and 4, $\phi = 5 \times 10^{-4}$ for line 5.

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on $Z$ first and then, the change of $Z^*$ is negligibly thin. It means that when $Z$ is rather small and $Z^* \approx Z$, there is practically no bound microions. Then $Z^*$ stops depending heavily on $Z$ and the number of the bound microions grows dramatically. We obtained the analogical dependence on the charge $Z$ for the dimensionless potential at the border of the macroion $e\varphi(R_Z)/(kT_i)$ (figure 3).

3. Difference in complex plasma thermodynamics when the linearization condition is used or not

In this section we consider reduced excess internal energy per one macroion

$$ u_{ex} = \frac{Ze}{2kT_i} \left( \varphi(r) - \frac{Ze}{r} \right)_{r \to R_Z}. \quad (8) $$

Khrapak et al [10] considered point-like macroions and microions ($R_Z = 0$). We obtained the dimensionless potential at the border of the macroion which is created by microions surrounding the macroion

$$ \frac{e\Delta \varphi(R_Z)}{kT_i} = \frac{e\varphi(R_Z)}{kT_i} - \frac{Ze^2}{R_Z kT_i}, \quad (9) $$

where $\varphi(R_Z)$ is the effective potential at the border of the macroion (figure 4). The abbreviation PB means that the potential $\varphi$ is obtained using the Poisson–Boltzmann equation (4). Also, we used two more potentials—LDH (linearized Debye–Hückel approximation) potential and the potential in the situation when all the microions have uniform profile (UP). We obtained these potentials in electroneutral cell like PB (see [14] for details). Thus, we have two more dimensionless potentials so that we subtracted $Ze^2/(R_Z kT_i)$ from LDH and UP potentials. The comparison of PB, LDH and UP potentials can be found elsewhere [14].

Earlier, Nefedov et al [19] proved that absolute value of potential created by a macroion and surrounding microions of two sorts, which was calculated as a function of distance using the
Figure 4. The dimensionless potential (at the border of the macroion) created by microions surrounding the macroion as a function of the macroion charge $Z$ ($n_Z = 10^8 \text{ cm}^{-3}$, $kT_i = 0.03 \text{ eV}$, $R_Z = 1 \mu \text{m}$, $R_Z/R \approx 0.075$). PB (solid black line 2), LDH (red line 5) and UP (blue line 6)—potentials when the corresponding function is used in (9) instead of $\varphi(r)$. We obtained green line 3 using the equation of state from [10]. Brown dashed line 4 (DHLL) corresponds to $\varphi(r) = Ze^2/(r_DkT_i)$. Black dashed line 1 corresponds to the potential $Ze^2/(R_ZkT_i)$ of charged sphere with the radius $R$ and absolute value of the charge $Z$.

linearization condition, is bigger than the potential which was obtained without this condition. They also wrote that the effective charge did not coincide with the real one. However, they did not show any dependences or consider thermodynamics in [19]. Also, we show Debye–Hückel limiting law (DHLL) dimensionless potential $Ze^2/(r_DkT_i)$ and potential of spherically-symmetric charged sphere $Ze^2/(R_ZkT_i)$ with the absolute value $Z$. The potential of a spherically-symmetric uniform charged ball $3Ze^2/(2RkT_i)$ practically coincides with UP potential in figure 4. The reason of this is the small value of the macroion radius in comparison with the value of the cell ($R_Z/R \approx 0.075$).

As $Z$ decreases, the Debye radius $r_D$ increases. In the case when $r_D$ is bigger than the cell radius $R$, line 4 (corresponds to DHLL potential) in figure 4 is lower than line 6 (corresponds to UP potential) for small $Z$. On the other hand, as $Z$ increases, $r_D$ decreases. When $r_D$ is the same as the macroion radius $R_Z$, the screening charge is located on the macroion surface (line 2 is approximated by line 1). When $r_D$ is smaller than the macroion radius $R_Z$, line 3 practically coincides with line 4 because $R_Z = 0$ for these lines.

Also, we obtained the reduced excess internal energy per one macroion using PB, LDH and UP potentials [it means that we used the corresponding potentials instead of $\varphi(r)$ in (8)]. We also calculated the reduced excess internal energies using the equation of state from [1, 3, 10]. The excess internal energy was used there to derive excess pressure. We showed in figure 5 that the absolute values of excess internal energies from [1,3,10] grow slowly than PB internal excess energy because Hamaguchi et al [1, 3] and Khrapak et al [10] used the Debye potential and so, the linearization condition. It leads to negative total pressure and negative total compressibility for not too big $\Gamma$ and $\kappa$. 
Figure 5. The reduced excess internal energy as a function of the macro ion charge in the case of $n_Z = 10^8$ cm$^{-3}$, $kT_i = 0.03$ eV, $R_Z = 1$ $\mu$m, $R_Z/R \approx 0.075$: (a) linear scale, (b) logarithmic scale; PB (solid black line 6), LDH (red line 2), UP (blue line 1) and DHLL (dashed brown line 3)—reduced excess internal energies if the corresponding potential is used in (8) instead of $\varphi(r)$. Violet line 4 with triangles is obtained using the results from [1] and [3]. We obtained green line 5 with filled circles using equation (18) and (19) from [10]. Black dashed line 7 is the reduced excess internal energy of the charged sphere.

4. Conclusions

We have calculated the reduced excess internal energy per one macroion, which had been derived in papers [1,3,10], using the Debye potential and the one obtained from the Poisson–Boltzmann equation in the cell without using the linearization condition. These internal energies are rather different. Total compressibility of the system was calculated earlier in [14] using the equations of state [1,3,10]. We guess that the difference in excess internal energies is one of the reasons of negative total compressibility in the phase diagram of complex plasma [1].
Moreover, we have demonstrated how the effective charge of the macroion \( Z^\ast \) changed as a function of real charge \( Z \). When \( Z \) is small there is practically no bound microions and then, when \( Z \) increases the number of the bound microions grows.

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