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Problem of phase transitions and thermodynamic stability in complex (dusty, colloid etc) plasmas

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Abstract. Features of the first-order phase transitions in complex (dusty, colloid etc) plasma are under discussion. The basis for consideration is the well-known phase diagram of dusty plasma as a Debye system from Hamaguchi *et al* (1997 *Phys. Rev.* E **92** 4671) in Γ–κ plane (Γ is a Coulomb non-ideality parameter, κ is a screening parameter). The initial Γ–κ phase diagram from Hamaguchi *et al* (1997 *Phys. Rev.* E **92** 4671) is converted in standard thermodynamic variables in temperature–density planes. Here 2-component electroneutral systems of macro- and microions $(+Z,-1)$ and $(-Z,+1)$ are considered as thermodynamically equilibrium ensembles of classical Coulomb particles. An extensive area for *negative compressibility* of the system was revealed at the phase diagram in a fluid state of the initial Debye system when one considers the system as equilibrium two-component electroneutral mixture of macro- and microions $(+Z,-1)$ (or $(-Z,+1)$) under equations of state from Hamaguchi *et al* (1997 *Phys. Rev.* E **92** 4671) and Khrapak *et al* (2014 *Phys. Rev.* E **89** 023102). This means thermodynamic instability of the simplified Debye system in this domain. Non-linear screening and an unavoidable existence of additional phase transitions of gas–liquid and gas–crystal type are proposed as hypothetical resolution of discussed thermodynamic instability problem.

1. Introduction

Various aspects of phase transitions in equilibrium complex plasma have been the subject of study in the last several decades. The thermodynamics of systems which are considered in this paper can be characterized in terms of two dimensionless parameters:

$$\Gamma = \frac{(Ze)^2}{Ta}, \quad \kappa = \frac{a}{r_D}, \tag{1}$$

where Γ is a parameter of non-ideality, κ is the ratio of the Wigner-Seitz radius $a = (3/4\pi n_z)^{1/3}$ to the Debye radius r_D. One of considered systems is discharged dusty plasma [1] ($\Gamma \sim 10^2$–10^4) which consists of macrocharges (here in other words macroions) with a charge number $Z \sim 10^3$–10^4, temperature $T_z \sim 1$–2 eV and concentracion $n_z \sim 10^5$–10^9 cm^{-3} and components of neutralizing background (in other words microions–electrons and ions) with $T_e \sim 1$–7 eV, $T_i \approx 0.03$ eV. We also consider one-temperature idealized colloid systems [2] with $Z \sim 10$–10^3, $\Gamma \sim 10$–10^3 and so-called CDP-plasma (with condensed dispersed phase) [3] with constant $Z \sim 10$–10^5, $\Gamma \sim 10$–10^5, $n_Z \sim 10^8$–10^{14} cm^{-3} and equal micro- and macroions temperatures.

One more considered system is dusty plasma in noctilucent clouds in the Earth's atmosphere [4] ($Z \sim 100$ and $T_e = T_z = T_i \approx 0.03$ eV, Γ is of the order of unity, $n_Z \sim 10$–10^3 cm^{-3}). The considered values of κ are ~ 0–10.

A well-known phase diagram of complex (dusty, colloid etc) plasma in Γ–κ plane [5] underlies the present paper. Molecular dynamic simulations were employed to obtain this diagram. A pair potential that describes interaction of two macroions is

$$\Phi(r) = \frac{(Ze)^2}{r}\exp(-r/r_D). \tag{2}$$

There are fluid, crystal bcc and crystal fcc phase states. All phase transitions are of the first-order. This implies that there is a first derivative discontinuity of a thermodynamic potential. Hamaguchi *et al* used isochoric conditions to obtain phase boundaries in [5] while it is well-known that one should equal not densities but pressures. Thus, we estimated a melting density gap in [6] and had $\Delta n/n \le 10\%$.

The paper is organized as follows. In Section 2 we correct some misprints of the previous paper [7] and convert the phase diagram of highly-asymmetric two-component (2C) electroneutral equilibrium systems $(+Z, -1)$ and $(-Z, +1)$ of classical macroions and microions into temperature–density plane. The systems are attractive (there is attraction between macro- and microions). In Section 3 we discuss a problem of thermodynamic stability and an appearance of negative total pressure and compressibility of equilibrium 2C models $(+Z, -1)$ and $(-Z, +1)$. Then we proceed with temperature and density applicability. Section 4 presents conclusions.

2. Phase diagram of an isothermal Debye system of macro- and microions $(+Z, -1)$ and $(-Z, +1)$

In this Section we consider two-component electroneutral equilibrium systems of macroions and microions $(+Z, -1)$ and $(-Z, +1)$ for simplicity and make the same assumptions as in [5]. The main idea of the present Section was also considered in [6, 7] but here we correct some misprints which we found out in figures 1–3 and 5 of [7].We use the Debye potential and the Debye radius

$$r_D = (4\pi n_{\rm micro} e^2/T_{\rm micro})^{-1/2} \tag{3}$$

depends on microions only like in [5, 8], (see formula (2) in [8]). Moreover, here we also consider isochoric conditions. In such a way a Debye radius $r_D(n_{\rm micro}, T_{\rm micro})$ doesn't depend on a phase state change of a macroions subsystem. It is obvious that in such a way $T_{\rm micro}$ and T_z are constant in phase transitions of the macroions subsystem. In this Section equal temperatures of all subsystems are considered. The electroneutrality condition is $Zn_Z = n_{\rm micro}$. Thus, taking in account (3) we have

$$\Gamma = Z^2 e^2 \Big(\frac{4\pi}{3}\Big)^{1/3} \frac{n_Z^{1/3}}{T}, \quad \kappa = \Big(3Ze^2\Big(\frac{4\pi}{3}\Big)^{1/3}\Big)^{1/2}\Big(\frac{n_Z^{1/3}}{T}\Big)^{1/2} \quad \Rightarrow \quad \Gamma = \frac{\kappa^2 Z}{3}. \tag{4}$$

It means that all *two-dimensional* T_Z–n_Z plane is equal to a parabolic curve $\Gamma \sim \kappa^2$ on the Γ–κ plane [5] for each fixed Z (see figure 1). There are different phase diagrams for different Z. Here we noticed some misprints and non-significant mistakes in the paper [7]. They were found in figures 1–3 and 5 there (figures 1–4 are revised versions in the present paper respectively). Now we present correct variants of the phase diagrams for $Z = 339$ (figure 2), 600 (figure 3), 1000 (figure 4). The phase diagram for $Z = 933$ can be found in [6]. One can notice a retrograde scenario of the phase diagrams. The system crystallizes and then melts as temperature decreases isochorically or density increases isothermally. The Debye radius (3) decreases in both cases and interactions disappear in the limit. It is valid for fluid. However, it is an artefact of the model. A

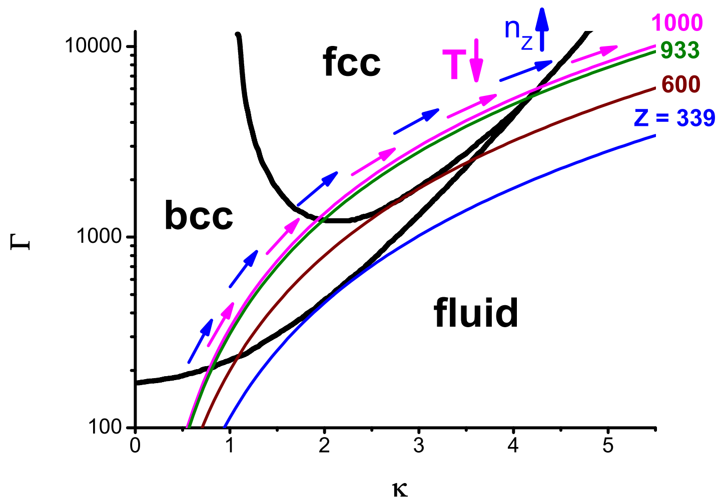

Figure 1. Phase diagram of a Debye system with boundary lines $Z = \text{const}$. The base is the phase diagram [5]. $Z = 339$: line $\Gamma \sim \kappa^2$ is a tangent to the fluid–bcc boundary. $Z = 600$: $\Gamma \sim \kappa^2$ is a tangent to the bcc–fcc boundary. $Z = 933$: $\Gamma \sim \kappa^2$ passes through the triple point fluid–bcc–fcc.

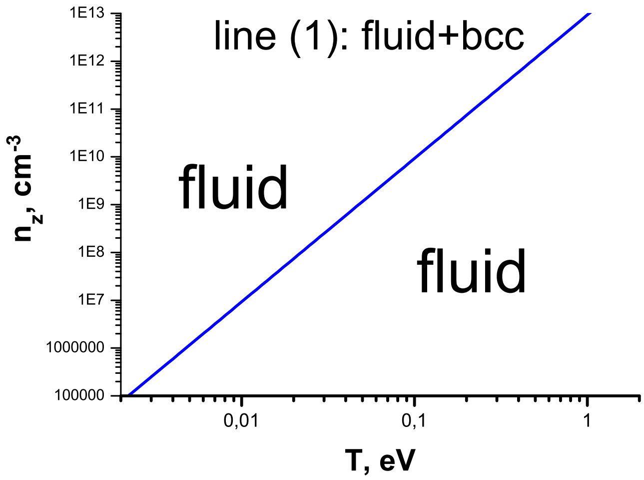

Figure 2. Phase diagram of a Debye system for $Z = 339$. Line (1): 2 phases coexist (fluid+bcc).

condition of linearization $Ze^2/rT \ll 1$, where r is a distance between a macro- and a microion, is not valid for low temperature. Thus, it is not a Debye screening in this case and nonlinear screening should be taken into account (see [3]). It leads us to a conclusion that the effective Debye potential is no more adequate in the limit of low temperature. Moreover, the density of macroions should be restricted above by the macroion excluded volume effect. Hamaguchi *et al* did not consider non-linear screening and the excluded volume effect. So, we are going to continue our researches in this field.

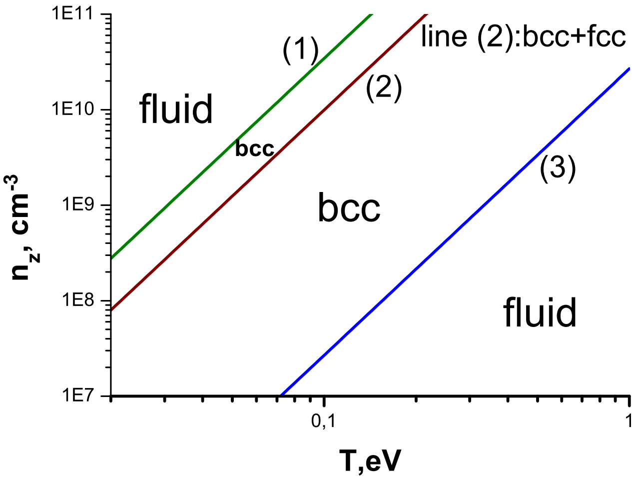

Figure 3. Phase diagram of a Debye system for $Z = 600$. Line (2): 2 phases coexist (bcc+fcc).

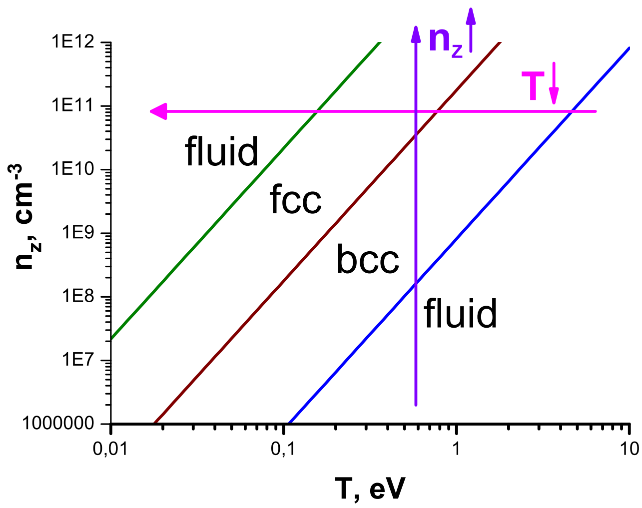

Figure 4. Phase diagram of a Debye system for $Z = 1000$.

3. Thermodynamic instability in two-component equilibrium Coulomb systems $(+Z, -1)$ and $(-Z, +1)$. Invalidity of the Debye potential

Some main quantities we will be dealing with in the following are total pressure P_{tot} and excess (non-ideal) part of pressure P_{ex}:

$$P = -\left(\frac{\partial F}{\partial V}\right)_T, \tag{5}$$

$$P_{\text{tot}} = P_{\text{id}} + P_{\text{ex}} = n_Z kT_Z + n_{\text{micro}} kT_{\text{micro}} + P_{\text{ex}}, \tag{6}$$

Table 1. Values of Γ and κ as fluid total pressure and fluid total compressibility become negative on the melting curve [5].

	$T_Z = T_{\rm micro}$	$T_Z = 1$ eV, $T_{\rm micro} = T_e = 7$ eV
negative compressibility	$\Gamma > 967$, $\kappa > 2.76$	$\Gamma > 960$, $\kappa > 2.78$
negative pressure	$\Gamma > 1295$, $\kappa > 3.05$	$\Gamma > 6352$, $\kappa > 4.35$

where F is free energy, $P_{\rm id}$ is an ideal part of pressure. Thus, we have

$$P_{\rm tot,fluid}/n_Z kT_Z = 1 + ZT_{\rm micro}/T_Z + P_{\rm ex,fluid}/n_Z kT_Z, \tag{7}$$

$$P_{\rm tot,crys}/n_Z kT_Z = ZT_{\rm micro}/T_Z + P_{\rm ex,crys}/n_Z kT_Z. \tag{8}$$

We concluded in our previous works [6] and [7] that ambiguity of an exact definition of a thermodynamic background role exists in the papers [5, 8, 9]. We considered fluid total pressure since only fluid equation of state was in [9].

Fluid total pressure and inverse fluid total compressibility $(\partial P/\partial n_Z)_T$ decreases and, finally, becomes negative as Γ increases on the melting curve, for example, see table 1 for [5], T_e is temperature of electrons for system $(+Z, -1)$!

The reason of the ambiguity lies in the following: background can be supposed incompressible like in [9] or compressible like in [5]. However, both ways should be examined. First of all, there are no volume variations as the background is incompressible. Thus, pressure (5) has no physical meaning. As for the second way to determine background, a system with negative total pressure must collapse. Moreover, there must be a phase decomposition as compressibility becomes negative.

We found out (see [6] for details) that there are huge areas of negative pressure and negative compressibility in the phase diagram [5] as one uses fluid equations of state [5, 9]. So, we expect a phase separation and it brings us to an existence of one more phase transition: gas–liquid and/or gas-crystal type.

A highly asymmetric ($Z/Z_{\rm micro} \gg 1$) equilibrium electroneutral Coulomb system which consists of macroions with finite sizes and point-like microions could be considered as the simplest model of real complex plasma. Panagiotopoulos *et al* used Monte-Carlo free energy calculations for the system mentioned above [10]. They showed that a phase separation is there. Futhermore, a phase transition with a significant density gap (gas–liquid type and gas–crystal type) exists at low enough temperature (see figure 1 in [10]).

A condition of linearization $Ze^2/\sigma T_{\rm micro} \ll 1$, where σ is a macroion diameter, is not valid for big enough Z in [5, 9]. For example, this conditioin is not valid for $Z > 22$ for the model $(-Z, +1)$, where $T_{\rm micro} = T_i = 0.03$ eV, $\sigma = 1$ μm as $Z = 10$ $Ze^2/\sigma T_i \sim 0.45$; as $Z = 22$ $Ze^2/\sigma T_i \sim 1$; as $Z = 100$ $Ze^2/\sigma T_i \sim 4.5 > 1$; as $Z = 1000$ $Ze^2/\sigma T_i \sim 45 \gg 1$.

It is also an artefact of the considered models. Although we made the same assumptions as in [5, 9] (i.e. a validity of the Debye potential), it means that the Debye potential is not adequate for a description of thermodynamics of two-component Coulomb systems. It is shown on figures 5–7 that the interaction between macroions in discharged dusty plasma, CDP-plasma and dusty plasma in noctilucent clouds stops being described by the Debye potential as Z increases. Thus, for example, as $Z = 1000$ the Debye potential is not adequate for a description of discharged dusty plasma representative region of existense. It is also seen that the density of the macroions subsystem is restricted above due to an impossibility to compress infinitely (isothermally) because of finite sizes of macroions.

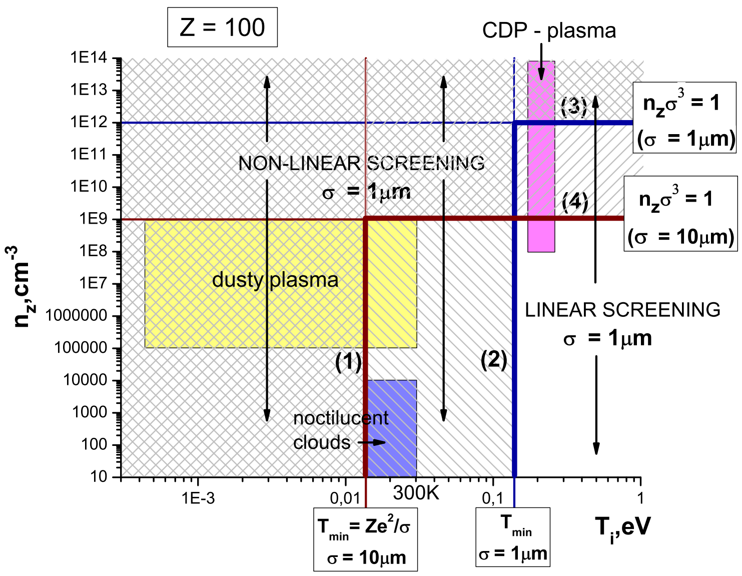

Figure 5. $Z = 100$. Linear screening boundaries $T_{\min}$ and density boundaries $n_{\max}$ (heavy lines (1) and (3) for a macroion with the diameter $\sigma = 1$ μm; heavy lines (2) and (4) for $\sigma = 10$ μm). Yellow, pink and blue rectangles are representative regions of existence of discharged dusty plasma, CDP-plasma and dusty plasma in noctilucent clouds respectively.

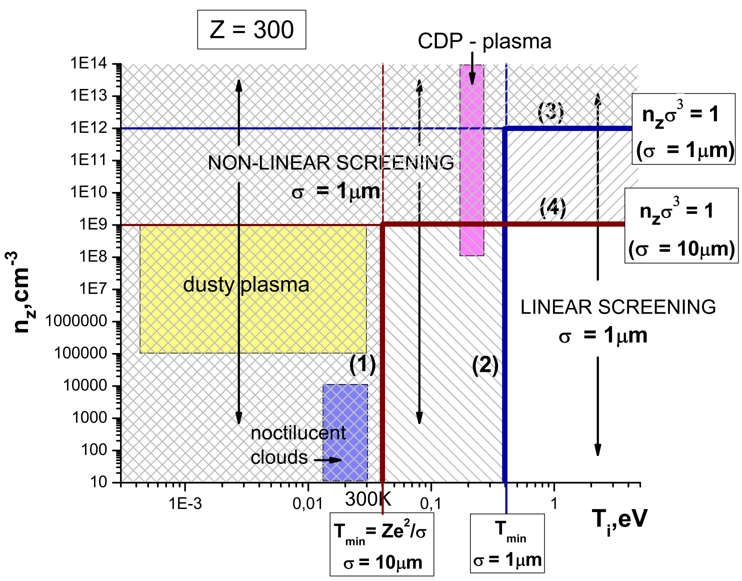

Figure 6. $Z = 300$. Linear screening boundaries $T_{\min}$ and density boundaries $n_{\max}$ (heavy lines (1) and (3) for a macroion with the diameter $\sigma = 1$ μm; heavy lines (2) and (4) for $\sigma = 10$ μm). Yellow, pink and blue rectangles are representative regions of existence of discharged dusty plasma, CDP-plasma and dusty plasma in noctilucent clouds respectively.

Moreover, the effect of nonlinear screening brings us to an effective renormalization of "visible" macroions charges like in [3]. After that Z will be smaller. The areas of negative

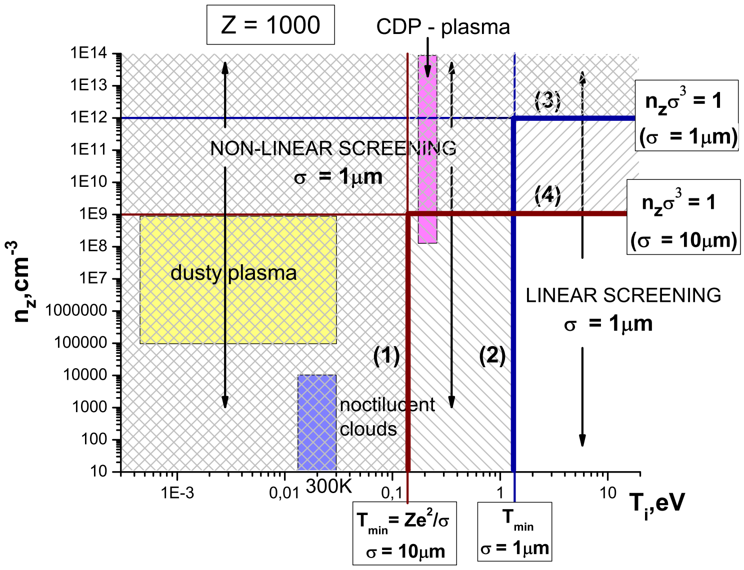

Figure 7. $Z = 1000$. Linear screening boundaries $T_{\min}$ and density boundaries $n_{\max}$ (heavy lines (1) and (3) for a macroion with the diameter $\sigma = 1$ μm; heavy lines (2) and (4) for $\sigma = 10$ μm). Yellow, pink and blue rectangles are representative regions of existence of discharged dusty plasma, CDP-plasma and dusty plasma in noctilucent clouds respectively.

pressure and compressibility will get smaller but they did not disappear in the limit. Thus, there is still an open question of negative pressure and negative compressibility appearance in the considered in [5, 9] models.

4. Conclusions

Well-known phase diagram in Γ–κ plane [5] of two-component equilibrium one-temperature complex plasma $(+Z, -1)$ and $(-Z, +1)$ under effective Debye potential was converted to more standard variables: temperature–density plane. The phase diagram in the new logarithmic plane has the form of an intermittent combination of linear fluid, bcc and fcc zones. It is surprising that fluid state is proved to be final at isothermal compression and/or isochoric cooling. This effect is claimed as artificial because another two effects which are important to an application to real complex plasma are not taken into account. First of all, it is a violation of linearized Debye approximation in the isochoric low temperature limit and coming of non-linear screening regime for macroions. Second, it is so-called excluded volume effect, i.e. an impossibility of a high isothermal compression of the system with finite sizes of macroions.

Debye potential is proved to be not adequate for a description of thermodynamics of attractive multi-component complex plasma due to apyee the condition of linearization for small enough values of the macroion charge number Z. One of the most unexpected results is a presense of almost all representative existence region of discharged dusty plasma, CDP-plasma and dusty plasma in noctilucent clouds beyond an area of valid linear screening for $Z \sim 100$. As for $Z = 1000$, all existence region of discharged dusty plasma and dusty plasma in noctilucent clouds are beyond this area. This effect leads to effective renormalization of "visible" charges of macroions in the fluid equations of state for attractive multi-component complex plasma [5, 9]. However, the main issue of these equations of state is an existence of extended regions of negative fluid total pressure and fluid total compressibility. This negativity is treated to be a direct indication of an existence of an additional phase transition of the first order (gas–liquid and/or gas–crystal) which were not taken in account in the initial paper [5]. Moreover, the phase transitions of this type were obtained by Panagiotopoulos *et al* who used Monte-Carlo direct simulations for highly asymmetric equilibrium electroneutral two-component Coulomb system of finite size macroions and point-like microions. Thus, the problem of thermodynamic stability should be examined carefully.

Acknowledgments

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