Phase transitions in local equation-of-state approximation and anomalies of spatial charge profiles in non-uniform plasma

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Abstract. Impressive appearance of discontinuities in equilibrium spatial charge profiles in non-uniform Coulomb systems is under discussions in wide number of thermoelectrostatics problems. Such discontinuities are considered as peculiar micro-level manifestation of phase transitions and intrinsic macro-level non-ideality effects in local equation of state (EOS), which should be used for description of non-ideal ionic subsystem in frames of local-density (or “pseudofluid”, or “jellium” etc) approximation. Such discontinuities were discussed already by the authors for electronic subsystems. Special emphasis is made in present paper on the mentioned above non-ideality effects in non-uniform ionic subsystems, such as micro-ions profile within screening “cloud” around macro-ion in complex (dusty, colloid etc) plasmas, equilibrium charge profile in ionic traps or (and) in the neighborhood vicinity of “charged wall” etc. Multiphase EOS for simplified ionic model of classical charged hard spheres on uniformly compressible electrostatic compensating background was constructed and several illustrative examples of discussed discontinuous ionic profiles were calculated.

1. Introduction

The “jellium” approximation i.e. replacing system of discrete particles, electrons and (or) ions, by hypothetical “fluid” with pure local properties (i.e. depending on local density only) is widely used not only in hydrodynamic applications but also in thermoelectrostatics i.e. in calculation of equilibrium charged particles distribution near a source of non-uniformity. The local equation of state (EOS), that connects local pressure, energy and chemical potential of charged particles with local density and temperature, is used for this purpose [1]. In most cases it is ideal-gas EOS based on “correlationless” Thomas–Fermi or Poisson–Boltzmann approximations (see e.g. [2]). The main problem of this approach is correct taking into account of mean-particle correlations (non-ideality). The simplest way to do it in frames of LDA (Local Dencity Approximation) is using of improved Thomas–Fermi–Dirac or Poisson–Boltzmann–Debye approximations (see e.g. [3, 4]). It was claimed already in early of number of early papers (see [5–7]) that obvious resolution
of this problem within LDA is replacing ideal EOS approximation by exact non-ideal EOS for one-component electronic (or ionic) subsystem.

2. Variational approach

It is well-known (see e.g. [2]) that any thermoelectrostatic problem can be formalized as a variational problem for the extremum of the thermodynamic potential (Helmholtz free energy) as a functional of the particle charge density \( n(r) \) under the constraint of electroneutrality:

\[
F = \min_{n(r)} F[n(r)] = Ze \int \phi_{\text{ext}}(\vec{x}) n(\vec{x}) d\vec{x} + \frac{Z^2 e^2}{2} \int \frac{n(\vec{x}) n(\vec{y})}{|\vec{x} - \vec{y}|} d\vec{x} d\vec{y} + F^*[n(\cdot)].
\]  

Here first and second terms are correspondingly the energy in external field (e.g. of nuclear in atomic cell) and Coulomb energy in “correlationless” mean-field approximation. The third term is a priori unknown exchange–correlation and kinetic term \( F^*[n(\cdot)] \). In widely used local thermodynamic equilibrium approximation (LTE) of the correlation and kinetic term we substitute a reduced local free energy \( f(n) \):

\[
F^*[n(\cdot), T] \approx \int f(n(\vec{x})) n(\vec{x}) d\vec{x}, \quad f(n) \equiv \lim_{N \to \infty, N/V = n} \left\{ \frac{F(N, V, T)}{N} \right\}. \]  

When \( F(N, V, T) \) is a free energy of ideal gas (Boltzmann or Fermi) we deal with correlation free Poisson–Boltzmann or Thomas–Fermi approximations. If \( F(N, V, T) \) is a free energy of one-component non-ideal gas with full interparticle correlations the third term of the functional becomes a free energy of OCP model on uniformly compressible background (see e.g. [6]).

3. Modified one-component plasma model with uniformly compressible background OCP(\( \sim \)).

Well-known classical one component plasma (OCP) is an idealized system of charge particles immersed in a uniform uncompressible “sea” of opposite charge such that whole system is electrically neutral (further notation is OCP(#)). The model exhibits only one phase transition (PT)—also well-known Wigner crystallization. This phase transition occurs without density change. In our previous studies [6–9] we introduced modified set of plasma models with common features—absence of individual correlations (coupling) between charges of opposite sign, and total compressibility of system (the following notation is OCP(\( \sim \))):

- classical point charges + background of ideal Fermi-gas of electrons;
- quantum interacting electron gas + positive electrostatic background;
- classical charged hard spheres + electrostatic compensating background [HS-OCP(\( \sim \))];
- “associationless” “Double-OCP” model—superposition of two OCP(\( \sim \)) of positive and negative charges with with equal or different masses (for example, electron–hole, electron–proton system).

It is also possible to provide the formal definition of the models. Here is the example of definition of the first type of models listed above (classical point charges with a compressible background of ideal Fermi-gas of electrons) [10]:

\[
(F/NkT)_{\text{OCP}(\sim)} = f_{\text{OCP}(\sim)} = f_{\text{id}} + \Delta f_{\text{int}} ii + (f_{\text{id}})_{ee} = (f_{\text{OCP}(\#)}) ii + (f_{\text{id}})_{ee},
\]  

where \( f_{\text{ee}} \) and \( f_{ii} \) are separate electron–electron and ion–ion terms of free energy with ideal \( f_{\text{id}} \) and nonideal \( \Delta f_{\text{int}} \) parts.

Uniform compressibility of background in the set of OCP(\( \sim \)) models leads to appearance of three standard phase transitions: melting, evaporation and sublimation (see [7]). Due to the model definition (absence of any individual subsystem-to-subsystem correlations such as ion–electron correlations) all parameters for the phase transitions (including parameters of spinodal
Figure 1. Phase diagram of OCP(∼) model of nonideal Fermi-gas of electrons: CP—critical point; dotted line—gas–liquid phase transition at particular temperature; 1—liquid branch; 2—gaseous branch; \( n_1^* \)—gas density; \( n_2^* \)—liquid density (figure from [7]).

Figure 2. Wigner–Seitz cell with discontinuous profile of electrons (schematic drawing): +Z—kernel charge; \( n_e(r) \)—profile of electron; \( n_1^* \)—gas density; \( n_2^* \)—liquid density (figure from [6]).

and metastable branches) can be obtained directly if properties of individual EOS, namely: OCP of ions with rigid background and ideal (or non-ideal) Fermi-gas of electrons are known.

It should be mentioned that the set of OCP(∼) models can provide important data (see [11]) to analyze results obtained in the dynamic experiments of reaching deep negative pressure in metastable stretched condensed matter in crystal and fluid states (see [12–14]).
4. OCP phase transition and anomalies in the equilibrium non-uniform charge distribution

The phenomenon which looks like phase transition in the OCP(∼) at macroscopic level, manifests itself at appropriate conditions (low enough temperatures and densities) at microscopic level as a discontinuity in equilibrium non-uniform charge profile. It occurs when simple local approximations of Thomas–Fermi–Dirac or Poisson–Boltzmann–Debye type already are used. In the previous studies we calculated the charge distributions in the following cases: electron profile in atomic cell [2, 3]. Taking into account e–e correlations in the local EOS of non-ideal electron gas means transition to EOS of OCP(∼) of non-ideal Fermi-gas of electrons on compressible electrostatic background in equation (2). At “low” enough temperature a gas–liquid phase transition appears in this OCP(∼) model (figure 1). Thus, at a temperature \( T < T_{\text{critical}} \) (\( T_{\text{critical}} \) is the critical temperature of the model) a discontinuity appears in electron profile in Wigner–Seitz cell: the profile breaks up into a dense condensed “drop” near the nucleus and a diffuse “atmosphere” in the rest of the cell (figure 2). In the present work we have studied additional cases:

- electron profile near the end of semi-infinite rigid positive background (the simplest model of metal surface) [15];
- counterion distribution around a polyion in electrolyte or free ions distribution around macroion in complex plasma (dusty, colloid etc see e.g. [16]).

In all the cases we have obtained the similar results. At sufficiently low temperatures (and densities) the predicted discontinuity appears in the charge profiles. In terms of the OCP(∼) phase transition this boundary temperature is just its critical temperature \( T_c \), and the two values of the local densities at the discontinuity are the coexisting densities of “condensed” and “gaseous phases”, which depend only on temperature.

5. Electron profile near a charged wall

A series of physical problems can be formalized as problem of calculation of an equilibrium profile of charged particles near a charged wall (permeable or not permeable). For example, simplest model of metal surface (“jellium model”) considers electron profile near the end of semi-infinite rigid positive background. If we try to take into account e–e correlations in local EOS during electronic profile calculation then we have to use exact non-ideal EOS in the density functional (1), (2), as well as in the previous example OCP(∼) model of Fermi-gas of electrons in a density functional. At low temperature the phase transition that exists in OCP(∼) model appears as a discontinuity in a profile of electrons (figure 3).

6. Polyion in electrolyte, colloid and dusty plasma or Z-pinch

Calculation of charge-distribution requires correct taking into account ion–ion correlation. A simple way of such correction in frames of LDA is substitution for ideal-gas (Boltzmann) dependence for the local charge density on the self-consistent pseudopotential in Poisson’s equation by exact EOS of non-ideal OCP of classical charged hard spheres system (HS-OCP) on compressible electrostatic background. The model equation of state can be obtained with the widely used approximation which represent the excess free energy as sum of the hard-core and electrostatic components, \( F_{hc} + F_{OCP} \) [17]. A lot of expressions for fluid and crystal hard spheres system free energy can be found in the literatures (see [18]). To represent electrostatic component we used so-called Mean Spherical Approximation (MSA) [16]. The HS-OCP(∼) model phase diagram exhibits all three standard phase transitions between gas, liquid and crystalline phases: melting, boiling and sublimation (solid–gas) (figure 4).
Figure 3. Electron profile near the end of semi-infinite rigid positive background: $T_c$—critical temperature of corresponding phase transition in OCP($\sim$) model of nonideal Fermi-gas; $n_e$—electron density; $x$—distance from surface in atomic units.

Figure 4. Phase diagram of HS-OCP($\sim$) model of charged hard sphere on a compressible electrostatic background: $T_c$—critical temperature; $n_c$—critical density.

There are set of applications where HS-OCP($\sim$) model of charged hard sphere can be used to replace Poisson–Boltzmann approximation:

- counterion distribution around a polyion in electrolyte;
- free ions distribution around macroion in dusty plasma;
Figure 5. Free microions distribution around macroion $Z_{\text{macroion}} = 10000e; T = 0.35T_{\text{cr}}$. Here $T_{\text{cr}}$—critical temperature of corresponding phase transition in HS-OCP(∼) model of charged hard sphere; $n_0$—critical density; $r_{\text{macroion}}$—macroion radius; $r_{\text{cell}}$—cell radius.

- ionic profile in Z-pinch–equilibrium quasistationary ensemble of classical “cold” ions around contracted “string” of relativistic electrons (see e.g. [1, 19]).

In all of these cases under particular conditions (low temperature and high charged particle density) a profile discontinuity can be observed. To illustrate discussed phenomenon we calculated ions distribution around macroion (figure 5). As we moved to non-ideal local equation of state we immediately run into “anomalies” in ion profile.

7. Conclusions
- In spite of the repulsion of like charges, taking into account individual charges correlations within the local density approximation is equivalent to an additional attraction, and therefore, the resulting charge profiles will be steeper in comparison with the profile calculated in “correlationless” approximation.
- At sufficiently low temperatures (even at small coupling parameter $\Gamma$), this effect could lead to dramatic change in the charged particles profile.
- The fact of the discontinuity appearance, as well as the parameters under which this takes place, receive a natural interpretation in terms of a phase transition in one-component plasma model OCP(∼) [5], which EOS replaces ideal gas equation of state in local density functional when we take into account charged particle correlations.

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