Pseudo-critical point in anomalous phase diagrams of simple plasma models

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Abstract. Anomalous phase diagrams in subclass of simplified (“non-associative”) Coulomb models is under discussion. The common feature of this subclass is absence on definition of individual correlations for charges of opposite sign. It is e.g. modified OCP of ions on uniformly compressible background of ideal Fermi-gas of electrons OCP(∼), or a superposition of two non-ideal OCP(∼) models of ions and electrons etc. In contrast to the ordinary OCP model on non-compressible (“rigid”) background OCP(#) two new phase transitions with upper critical point, boiling and sublimation, appear in OCP(∼) phase diagram in addition to the well-known Wigner crystallization. The point is that the topology of phase diagram in OCP(∼) becomes anomalous at high enough value of ionic charge number \( Z \). Namely, the only one unified crystal-fluid phase transition without critical point exists as continuous superposition of melting and sublimation in OCP(∼) at the interval \( (Z_1 < Z < Z_2) \). The most remarkable is appearance of pseudo-critical points at both boundary values \( Z = Z_1 \approx 35.5 \) and \( Z = Z_2 \approx 40.0 \). It should be stressed that critical isotherm is exactly cubic in both these pseudo-critical points. In this study we have improved our previous calculations and utilized more complicated model components equation of state provided by Chabrier and Potekhin (1998 Phys. Rev. E 58 4941).

1. Introduction

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 of the model is OCP(#). The model exhibits only one phase transition (PT)—again well-known Wigner crystallization. This phase transition occurs without any density change. In our several previous studies [1–5] we introduced slightly modified set of plasma models with common features—absence of individual correlations (coupling) between charges of opposite sign, and total compressibility of system. The simplest example of such a system is OCP of classical point charges with a compressible background of ideal Fermi-gas of electrons. We will use the following notation OCP(∼) to denote these models further. The model formal definition is [6]:

\[
\left( \frac{F}{NkT} \right)_{OCP(\sim)} = f_{OCP(\sim)} = (f_{id} + \Delta f_{int})_{ii} + (f_{id})_{ee} = (f_{OCP(#)})_{ii} + (f_{id})_{ee}.
\] (1)
It is also possible to introduce more realistic and complicated system of two OCP-s immersed in each other. In other words this is superposition of two non-coupled OCP-s of mass-non-symmetrical charged particles of opposite sign. As in the previous case the “double” OCP(\sim) model (DOCP) still does not include any individual ion-electron correlations. Formally we can define this variant of OCP(\sim) as follows:

\[ (F/NkT)_{DOCP} = f_{DOCP} = f_{ii} + f_{ee} = (f_{OCP(#)}_{ii}) + (f_{OCP(#)}_{ee}). \]  

(2)

Uniform compressibility of background in the set of OCP(\sim) models leads to appearance of three standard phase transitions: melting, evaporation and sublimation. The absence of any individual ion-electron correlations (definition of the models doesn’t include electron-ionic term \( f_{ei} \)) in the discussed models dramatically reduce the complexity of the calculations and all parameters for the phase transitions (including parameters of spinodal and metastable branches) can be obtained directly if properties of two individual subsystems, namely: OCP of ions with rigid background and ideal (or non-ideal) Fermi-gas of electrons are known.

2. Phase diagrams topology in OCP(\sim)
One of the methodical advantages of the OCP(\sim) model is additional model parameter: charge of ions \( Z_i \). Topology of a phase diagram fully depends on it.

We can distinguish four qualitatively different situations for the OCP(\sim) depending on the value of charge number \( Z \):

(i) classical phase diagram with upper critical point—low value of charge number: \( Z < Z^*_1 \);
(ii) anomalous crystal-crystal phase diagram—high value of charge number: \( Z > Z^*_2 \);
(iii) anomalous phase diagram without the critical point—intermediate value of charge number: \( Z^*_1 < Z < Z^*_2 \);
Figure 2. (From the left) Anomalous $n-T$ phase diagram in the OCP($\sim$) model at $Z = Z_1^{*}$: $T_c$ and $n_c$ temperature and density of pseudocritical point; 1—binodal of global crystal-fluid transition as superposition of melting at $T > T_c$ and sublimation at $T < T_c$; 2, 4 and 6—binodal, spinodal and critical point of metastable crystal-crystal transition; 3, 5 and 7—binodal, spinodal and critical point of metastable gas-liquid transition; 8—melting line ($\Gamma \approx 175$) in prototype model OCP(#) 7—the pseudocritical point at $Z = Z_1^{*}$ on bimodal (1).

Figure 3. (From the left) Anomalous $n-T$ phase diagram in the OCP($\sim$) model at $Z = Z_2^{*}$: same as in figure 2; except for 6—the pseudocritical point at $Z = Z_2^{*}$ on bimodal (2).

(iv) anomalous phase diagram where boundaries of melting stripe touch the critical point—boundary value of intermediate charge number interval: $Z = Z_1^{*}$ and $Z = Z_2^{*}$. The actual values of $Z_1^{*}$ and $Z_2^{*}$ slightly depends on particular model EOS-s.

The all mentioned types of the diagrams are depicted in the figure 1.

3. Anomalous phase diagram at boundary values of charge number interval: $Z = Z_1^{*}$ or $Z = Z_2^{*}$

Notable feature of phase diagram of OCP($\sim$) model is an existence of pseudo-critical point where the well-known standard conditions are fulfilled (see figure 2 and figure 3):

$$\left. \frac{\partial P}{\partial V} \right|_T = 0 \quad \text{and} \quad \left. \frac{\partial^2 P}{\partial V^2} \right|_T = 0.$$  \hfill (3)

As mentioned above this type of topology is a result of touching MMT (metastable melting termination point—the end of melting stripe due to crossing spinodal [8]) and phase diagram critical point. $Z = Z_1^{*}$ or $Z = Z_2^{*}$ correspond to the event when melting stripe freezing boundary or melting boundary touch the critical point. When we use the same as in [2–5] analytical fits for equation of state of OCP($\sim$) model, we obtain the following parameters of the both pseudo-critical points (table 1).
3.2. Saturation curve

Similar violation is observed for saturation \( P(T)_{st} \) curve. So-called Plank-Gibbs rule (equal slope of saturation curve at \( T = T_c - \varepsilon \) and critical isochor at \( T = T_c + \varepsilon \) is valid for an ordinary critical point:

\[
\left. \frac{dP}{dT} \right|_{st} = \left. \frac{\partial P}{\partial T} \right|_{v_c}.
\]

It is not evident (see figure 5), but it can be proved that this rule is not valid for pseudo-critical points \((Z = Z_1^* \text{ or } Z = Z_2^*)\).

4. General characteristic of anomalous phase diagrams

Anomalous phase diagram with an unique phase equilibrium crystal-fluid is not an exclusive feature of OCP\((\sim)\) model. This behavior is quite common for systems with traditional interparticles interaction which combines intensive shot-range repulsion and finite in depth and spread attraction. For instance transition from “normal” phase diagram to anomalous one has been observed in one-component system of hard spheres with additional short-range Yukawa like attraction \([12]\). Analytical and numerical modeling of this system along with experimental results (large colloidal particles in polymer solution) show the effect qualitatively the same one in OCP\((\sim)\) model when ions charge \(Z_i\) tend to the interval \([Z_1^* \div Z_2^*]\). That is gradual closing triple and the critical points right up to their merging and formation a single crystal-fluid phase boundary.

Table 1. Parameters of pseudo-critical point in OCP\((\sim)\): I: OCP\((\sim)\)–classical point charges on the uniform and compressible background of ideal Fermi-gas of electrons (EOS-s are from \([9,10]\)); II: DOCP–classical point charges on the uniform and compressible background of nonideal Fermi-gas of electrons (EOS-s are from \([11]\)); \(\Gamma \equiv kT/\varepsilon_F = 4/(9\pi)^{1/3}(n_e\Lambda_e^3)^{2/3}, \Lambda_e^2 \equiv 2\pi\hbar^2/m_e kT, a_j \equiv (4\pi n_j/3)^{-1/3}\).

| \(Z\) | \(T_c, \text{a.u.}\) | \((n_c)_{c, cc^{-1}}\) | \(P_c, \text{a.u.}\) | \(\Gamma_c\) | \((r_s)_{c}\) | \((n_e\Lambda_e^3)_{c}\) | \((\Theta)_{c}\) |
|------|----------------|----------------|----------------|--------|-----------|---------------|------------|
| I \(Z_1^*\) | 38.4 | 7.30 | 2.79 \times 10^{25} | 15.7 | 155 | 0.387 | 3.30 | 2.91 |
| \(Z_2^*\) | 50.0 | 10.6 | 4.84 \times 10^{25} | 39.5 | 199 | 0.322 | 3.26 | 2.89 |
| II \(Z_1^*\) | 40.5 | 8.70 | 3.63 \times 10^{25} | 24.6 | 155 | 0.354 | 3.30 | 2.91 |
| \(Z_2^*\) | 51.6 | 12.1 | 5.86 \times 10^{25} | 55.0 | 196 | 0.301 | 3.27 | 2.89 |
Figure 4. (From the left) Critical exponents at $Z = Z_1^*$: density $\leftrightarrow$ temperature diagram; $T_c$ and $n_c$—temperature and density of pseudocritical point; 1—binodal of global crystal-fluid transition at $T < T_c$ (see figure 2); 2 and 3—binodal and spinodal of metastable gas-liquid transition; 4—$(\rho - \rho_c) \sim |T - T_c|^{1/3}$, 5—$(\rho - \rho_c) \sim |T - T_c|^{1/2}$.

Figure 5. (From the right) Saturation curve at $Z = Z_1^*$: pressure $\leftrightarrow$ temperature diagram; $T_c$, $P_c$ and $v_c$ temperature, pressure and specific volume of pseudocritical point; 1—binodal of global crystal-fluid transition $T < T_c$ (sublimation); 2—binodal of global crystal-fluid transition $T > T_c$ (melting); 3—crystal isochor ($v < v_c$); 4—gaseous isochor ($v > v_c$); 5—critical isochor ($v = v_c$); 6—pseudocritical point.

Figure 6. (From the left) Phase diagram [12] of hard particles with Yukawa potential: circles •—TTB calculation, dotted line—numeric calculation.

Figure 7. (From the center) Phase diagrams [13] for colloid charges $Z_i = 10$: circles ○—MC simulation, circles •—approximate calculations, the stars *—the critical points.

Figure 8. (From the right) Isostructural crystal–crystal phase transition with upper critical point in cerium (phase diagram [14]).
The results of phase diagram calculations for the model of hard particles with Yukawa potential [12] and charged hard spheres model [13] are shown on the figure 6 and figure 7 respectively.

The phase diagram similar to OCP(∼) diagram for larger \( Z_i \) has been observed even in real substance [14] (figure 8).

5. Conclusion

The current analysis based on the “non-associative” Coulomb models shows the common features of phase transitions in a pure Coulomb systems. A modified OCP models let us directly calculate a set of anomalous phase diagrams with non-standard topologies of phase boundaries: continuous infinite superposition of boiling and sublimation boundaries and absence of the critical points; special cases related to pseudo-critical points. It should be emphasized that the models and all findings are based on the “first principles” because all calculations utilize results of direct Monte Carlo or MD simulations. Thus we can expect that anomalous phase diagrams are quite common phenomena in idealized Coulomb systems with high values of charge number \( Z \). The recent publications (e.g. [13]) confirm this assumption and we see “non-standard” topologies of phase boundaries in other Coulomb modeling systems and even in real matter (e.g. [14]). Thus the exotic pseudo-critical points that have been precisely calculated in this study based on widely used equation of state [11] can also be found in those Coulomb systems.

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