Triple point of “shelf Coulomb” plasma model calculated using hybrid Gibbs ensemble technique

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Abstract. Previously, a two-component pseudopotential “shelf Coulomb” plasma model has been developed. A Monte-Carlo study of canonical NVT ensemble with periodic boundary conditions has been performed to find gas–liquid critical point in the model. In present work additional calculations have been carried out using hybrid Gibbs statistical ensemble Monte-Carlo technique. New data for 15kT shelf has been obtained and presented in this paper. More accurate simulations confirmed the melting curve position and triple point estimations of the model ($T^* \approx 0.0476$, $v^* \approx 6 \times 10^{-4}$).

1. Introduction
A “shelf Coulomb” model for systems of particles interacting via Coulomb law has been studied recently. This model was initially proposed and successfully used as a basic model for the pseudopotential approximation of strongly coupled two-component non-degenerate plasma in [1–3]. Equilibrium properties and distribution functions in two-component low temperature plasmas were calculated using pseudopotential approximation and “shelf Coulomb” model by Monte-Carlo technique [4], gas–liquid type phase transition was found [5].

Present model is different from other two models widely used for studies of Coulombic systems. The first one is a system of charged classical particles, which move in a uniform positive neutralizing background, known as one-component plasma (OCP) model [6–8]. It is usually utilized to study thermodynamics of liquid metals and dense degenerated plasmas. The second model is a charged hard sphere model [6–13], also known as the restricted primitive model (RPM), utilized for studies of electrolytes.

1.1. The model and “gas–liquid” phase transition
This model is defined by interaction pseudopotentials between charged particles of two kinds (electrons and ions) as follows:

$$\beta \Phi_{ee}(x) = \beta \Phi_{ii}(x) = x^{-1},$$

$$\beta \Phi_{ee}(x, \beta) = \begin{cases} -\varepsilon, & \text{if } x \leq \varepsilon^{-1}, \\ -x^{-1}, & \text{if } x > \varepsilon^{-1}, \end{cases}$$

(1)

where $x = r/\beta e^2$, $r$—distance between particles, $\beta = 1/k_B T$, $k_B$—Boltzmann constant, $e$—elementary charge, $T$—temperature (Kelvin).
Figure 1. Typical densities histogram and densities evolution for low $\gamma$ values for $T^* = 1/15$—below gas–liquid critical point, near spinodal line of the gas phase. Simulation boxes tend to evolve to different phases.

Figure 2. Densities histogram and densities evolution for low $\gamma \approx 3.6$ values for $T^* = 1/15$—below gas–liquid critical point. The $\gamma$ value is in the region where crystal like phase is expected to emerge, simulation boxes clearly evolves into two different phases.

To put it differently, a classical Coulomb potential is used as an interaction pseudopotential between like-charged particles, whereas “cut off” Coulomb potential is used as an interaction potential between oppositely charged particles. The “cut off” distance (or shelf size) as well as the “cut off” depth (or shelf potential depth) is determined by an arbitrary $\varepsilon$ parameter.

It is usual way to use dimensionless parameters in the model as follows: $\gamma = \beta e^2 n^{1/3}$—nonideality parameter ($n$—particle density), $v^* = 1/\gamma^3$—reduced specific volume, $P^* = \beta P (\beta e^2)^3$—reduced pressure, $T^* = 1/\varepsilon$—reduced temperature.

Phase properties of the model have been investigated and the critical point and binodal lines were found for this model [5]: $P_{\text{crit}}^* \approx 0.39$, $v_{\text{crit}}^* \approx 0.17$ ($\gamma_{\text{crit}} \approx 1.8$), $T_{\text{crit}}^* \approx 1/13 \approx 0.076$. 
2. Liquid–crystal type phase transition

Results presented in this work refine previous data and confirm previous estimations. New data for 15kT shelf is presented.

So called hybrid Gibbs ensemble technique [14–20] was used for “shelf Coulomb” model to determine the liquid–crystal phase diagrams without any prior knowledge of whether this kind of phase transition exists or not. Previous results [12] were used as a starting point of discovering higher γ region. The Gibbs ensemble consisting of 728 electrons and 728 protons was split on...
two equal volumes and the system was observed to evolve to different states. Additional data was obtained for 15kT shelf.

As one can see in figures 1 and 2, the system clearly splits to two different phases both in the gas–liquid and solid-liquid regions. Because of the $T^*$ parameter is below the gas–liquid critical point [12] we may assume that we found (at least qualitatively) the region of a liquid–crystal phase equilibrium.

System exhibits different behavior when $\gamma$ is near melting curve.

As one can see on figure 3, system behaves differently on the melting curve as opposed to gas–liquid phase region. One of the Gibbs ensemble simulation boxes collapses and the only dense phase exists. Occasionally two simulation boxes may switch the phases, meaning that all the particles flow from one box to another and form the same phase of the same density.

As one can see from the histogram the system tends to stuck in one definite density value. Structure observations show that this phase radial distribution functions have long range correlations.

Extrapolating the melting curve to lower temperatures we may estimate the triple point parameters as well as shown in figure 4, where the points from figures 1–3 and additional phase diagram data [14] are plotted together.

3. Conclusion
Previously reported results [14] are confirmed and clarified. New calculations made for 15kT shelf show the formation of a crystal phase in the expected region. Additional evidence and rough estimation of liquid–crystal phase transition parameters of the “shelf Coulomb” model are obtained.

One should note that current results although quite interesting and new, are still being improved and clarified. More thorough investigation of different regions together with the hybrid Gibbs ensemble method applicability itself are required and to be made. For example, it is not yet clear what types of lattice is formed in the crystal region of the system.

Using the Gibbs ensemble technique for analysis of liquid–crystal phase transitions has never been made before (to our knowledge) and it seems to give non-controversial results for our Coulomb model.

And it let us to get rough estimation of the triple point: $T^* \approx 0.0476 (\varepsilon \approx 21kT), v^* \approx 6 \times 10^{-4}$ ($\gamma \approx 11$).

Acknowledgments
The work is supported by the Russian Science Foundation (grant 14-19-01492).

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