Calculating phase equilibrium properties of plasma pseudopotential model using hybrid Gibbs statistical ensemble Monte-Carlo technique

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Abstract. Earlier a two-component pseudopotential plasma model, which we called a “shelf Coulomb” model has been developed. A Monte Carlo study of canonical NVT ensemble with periodic boundary conditions has been undertaken to calculate equations of state, pair distribution functions, internal energies and other thermodynamics properties of the model. In present work, an attempt is made to apply so-called hybrid Gibbs statistical ensemble Monte-Carlo technique to this model. First simulation results data show qualitatively similar results for critical point region for both methods. Gibbs ensemble technique let us to estimate the melting curve position and a triple point of the model (in reduced temperature and specific volume coordinates): \( T^* \approx 0.0476, \ v^* \approx 6 \times 10^{-4} \).

1. Introduction

There are two theoretical models widely used for studies of Coulomb systems. A system of charged classical particles, which move in a uniform positive neutralizing background, is known as one-component plasma (OCP) model [1–3]. It is usually utilized to study thermodynamics of liquid metals and dense degenerated plasmas. In addition, a charged hard sphere model [4–8] also known as the restricted primitive model (RPM), utilized for studies of electrolytes.

On one hand, these models are used to describe real systems, but on the other hand, it is interesting matter to study by itself. Because these models represent systems of many particles where numerous physical and statistical phenomena take place (e.g. phase transitions).

There is another model for systems of particles interacting via a Coulomb law—so called “shelf Coulomb” model. This model was initially proposed and successfully used as a basic model for pseudo-potential approximation of strongly coupled two-component non-degenerate plasmas in [9–11]. Equilibrium properties and pair distribution functions of two-component low temperature plasmas were calculated using pseudo-potential approximation and “shelf Coulomb” model with Monte Carlo technique [12].

This model is defined by interaction potentials between charged particles of two kinds (electrons and ions) as follows:

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

\[
\beta \Phi_{ee}(x, \beta) = \begin{cases} 
-\varepsilon, & x \leq \varepsilon^{-1} \\
-x^{-1}, & x > \varepsilon^{-1} 
\end{cases}
\]
where \( x = r/(\beta e^2) \), \( r \) — distance between particles, \( \beta = 1/(k_B T) \), \( k_B \) — Boltzmann constant, \( e \) — elementary charge, \( T \) — temperature (degrees Kelvin). It is important to note that this formal temperature dependence of the potentials has nothing to do with any real interparticle interaction. This model represents pseudo–potentials that are visual representations of correspondent two–particle partition functions. Temperature dependence of a partition function is taken into account when thermodynamical properties are calculated using Monte–Carlo technique. See [9–12] for details.

In other words, a classical Coulomb potential is used as an interaction potential 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.

Because of all the equilibrium properties for given \( \varepsilon \) depend only on \( \gamma = \beta e^2 n^{1/3} \) (\( n \)—particles density) interaction parameter, its appropriate to introduce new reduced variables and switch to using them in our further analysis: reduced specific internal energy \( E^* = \beta E/N \), reduced pressure \( P^* = \beta P(\beta e^2)^3 \), specific volume (volume per particle) \( v^* = 1/\gamma^3 \), reduced temperature \( T^* = \varepsilon^{-1} \).

Critical point and binodal lines were found for this model [12]:

\[
P^*_{\text{crit}} \approx 0.39, \quad v^*_{\text{crit}} \approx 0.17 \quad (\gamma_{\text{crit}} \approx 1.8), \quad T^*_{\text{crit}} \approx 1/13 \approx 0.076.
\]

### 2. Liquid–crystal type phase transition

Our next goal is to find the liquid–crystal type phase transition that we assume to exist in “shelf Coulomb” model. But approach used in [12] for determining gas–liquid critical point (obtaining internal energy and pressure from Monte-Carlo NVT ensemble simulation) does not give reliable data for larger values of interaction parameter \( \gamma \) where liquid–crystal phase transition is expected.

New idea was to try so called hybrid Gibbs ensemble technique [13] 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.

To our current knowledge, there are no works that utilize this technique for studying liquid–crystal type phase transitions, as well as no solid evidence that it may not be possible. The present work in this sense may be considered as a sort of verification of the methods applicability to liquid–crystal type phase transitions in Coulomb systems.

The hybrid Gibbs ensemble method initially proposed in [13] became widely adopted to determine phase coexistence properties of different systems. The method involves performing a simulation in two distinct but coupled regions with generally different densities and compositions in a way that ensures the criteria for phase equilibrium, equality of temperature, pressure, and chemical potentials of all components in the two phases, are satisfied in a statistical sense.

The method has been used to predict vapor–liquid, liquid–liquid, and osmotic equilibria for binary Lennard–Jones mixtures [14], phase transitions for fluids in pores [15], equilibria for quadrupolar fluids [16], liquid–vapor phase transition of the restricted primitive model of ionic fluids [17] etc.

There are known difficulties [17] of methods application to coulombic systems:

- Low ratio of accepted Monte-Carlo steps for low temperatures (which is equivalent to high coupling or big \( \gamma \) parameter values in “shelf Coulomb” system)
- Numerical simulation results become very unstable due to large fluctuations of averages near the critical point

The first issue may be solved in some extent by introducing custom particles transition algorithms optimized for improving the acceptance ratio in Monte-Carlo steps [17].
The second issue makes it hard to distinguish two phases of the system in numerical experiment and therefore to define the point where system tends to split on two phases. Histograms approach was used in [18] to visualize the evolution of the system—to see which phases system tends to evolve to during a Monte-Carlo simulation.

3. Results for “shelf Coulomb” model

Previous results [12] were used as a starting point of discovering higher $\gamma$ 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.

As you see on figures 1 and 2, with increasing $\gamma$ parameter values system evolves from single phase weakly coupled plasma to the state where two separate phases with different densities coexist in equilibrium. Because of the $T^*$ parameter is above the gas–liquid critical point.
Figure 3. Typical densities histogram and densities evolution for low $\gamma$ values for $T^* = 1/12$ ($\varepsilon = 12k_B T$)—near gas–liquid critical point. Both simulation boxes contain the same phase.

Figure 4. Densities histogram and densities evolution for $\gamma \approx 11$ for $T^* = 1/12$ ($\varepsilon = 12k_B T$)—near gas–liquid critical point. The minimal $\gamma$ value where simulation boxes clearly evolves into two different phases.

[12] we may assume that we found (at least qualitatively) the region of a liquid–crystal phase equilibrium.

System exhibits similar behavior when $T^*$ is near gas–liquid critical point.

As you see on figures 3 and 4 system behaves pretty much the same as for higher $T^*$. We may plot the given densities on the phase diagram for gas–liquid phase transition [12].

Which gives us an estimation of a triple point and shows the melting curve. As you see on figure 5 where the densities points from figures 1–4 along with $v_{\text{shelf}}^*$ (the volume of the coulomb potential “shelf” cut-off length) are plotted.

The melting curve is near the $v_{\text{shelf}}^*$ curve which means melting starts when average inter-particle distance in the system is about or less than a coulomb potential cut-off (“shelf”) size in the model. Extrapolating the melting curve to lower temperatures we may obtain estimation for the triple point parameters as well.
4. Conclusion

It is important to emphasize 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 are being made. The structure of a “crystal” phase should be inspected carefully, because (as our 3D visualizations show) it is never an ideal crystal that is forming during Monte–Carlo simulation, but more or less ideal crystal–like structure with long–range order radial distribution function.

Motivation behind current phase of work is to get some evidence and rough estimation of liquid–crystal phase transition parameters of the “shelf coulomb” model with no need to get precise numbers nor to compare to any experimental data. The purpose is to develop our understanding of the “shelf Coulomb” model itself.

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 a triple point: $T^\ast \approx 0.0476$ ($\varepsilon \approx 21k_B T$), $v^\ast \approx 6 \times 10^{-4}$ ($\gamma \approx 11$). The considered model can be applied to extend the results of works [19–22].

Acknowledgments

The work is supported by the Russian Science Foundation, grant No. 14-19-01492.

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