Gas–liquid phase transition in modified pseudopotential and “shelf Coulomb” ultracold plasma models

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Abstract. Phase diagrams for the “shelf Coulomb” and the modified pseudopotential plasma models developed in our previous works are compared. Qualitative agreement is observed between gas–liquid phase transition region of “shelf Coulomb” model and liquid–gas structure region of modified pseudopotential one. The possibility of experimental finding of the phase transition in nonequilibrium ultracold Rydberg plasma is considered. Parameters (density, temperature, levels of Rydberg atoms) for such a transition are estimated. Conclusion is made that “shelf Coulomb” model phase transition is practically impossible to observe in equilibrium strongly coupled plasmas due to high neutral atoms density at low temperatures: \( T^{\ast \ast}_{\text{crit}} \approx 0.076 \).

1. Introduction
It is known that the main interaction between particles in strongly or fully ionized plasma is a charge interaction according to the Coulomb law [1]. The ratio of the Coulomb interaction at a mean particle–particle distance to the temperature is determined by the Coulomb nonideality parameter \( \gamma = \beta e^2 n^{1/3} \), where \( e \) is the elementary charge, \( n_e \) is the electron concentration, \( n_i \) is the ion concentration, \( \beta = 1/k_B T \), \( k_B \)—Boltzmann constant, \( T \)—temperature (Kelvin).

In present work two similar approaches to calculating thermodynamic properties of strongly coupled plasma are compared. The first one is the pseudopotential model, initially proposed in [2, 3] and explored in detail later [4, 5]. The other one is so called “shelf Coulomb” model, proposed in the same works [2–4], developed in [6, 7].

2. Pseudopotential model results
To characterize comprehensively the thermodynamics of a quantum-mechanical system, we need to know the statistical sum represented as

\[
Z_N = S p(\exp(-\beta \hat{H})) = \int_{V_N} \sum_{n=1}^{N} |\Psi_n|^2 \exp(-\beta E_n) d^N q,
\]

(1)

where \( \Psi_n \) and \( E_n \) are the wave functions and energy levels of \( N \) particles, \( \hat{H} \) is the Hamiltonian of the system consisting of \( N \) particles, \( q \) are the coordinates of \( N \) particles, and \( V \) is the volume of the system.
The idea of the pseudopotential model is as follows. The Slater sum is
\[
S_N = N! \lambda^3 \sum_{n=1}^{\infty} |\Psi_n|^2 e^{-\beta E_n}.
\] (2)

Here, \( \lambda \) is the thermal wavelength of a particle. The Slater sum is represented as a product of the pair (electron–electron, ion–ion, and electron–ion) Slater sums:
\[
S_{N_e+N_i} = \prod_{i<j=1}^{2N} S_{ij} = \prod_{i<j=1}^{N_e} S_{ee} \times \prod_{i<j=1}^{N_i} S_{ii} \times \prod_{i<j=1}^{N=N_e+N_i} S_{ei}.
\] (3)

By analogy with the classical analysis, we can substitute the expression
\[
S_{N_e+N_i} = \exp(-\beta \sum U_{ij}),
\] (4)

where the pseudopotential is given by
\[
U_{ij} = -\ln(S_{ij})/\beta
\] (5)
for the above product.

One can exactly calculate the pair Slater sums for electron–ion \((S_{ei})\), electron–electron \((S_{ee})\), and ion–ion \((S_{ii})\) interactions \([8, 9]\). At large distances, the pseudopotential coincides with the Coulomb potential. At small distances, the pseudopotential is finite and temperature-dependent.

Important modification of the Slater sum calculation is to eliminate some lower levels of Rydberg atom spectrum from the sum. This leads to pseudopotential depending on the temperature and on the number of level taken into account. This is called a modified pseudopotential model for strongly coupled plasma. A couple examples of different pseudopotentials for different levels included and temperatures are shown in figure 1.

In the framework of the pseudopotential approach, the quantum-statistical sum is reduced to an expression resembling the classical one. Therefore, to find the corresponding thermodynamic quantities, we can employ all the methods (both analytical and numerical) that have been developed in the statistical thermodynamics of classical systems. Thermodynamic properties and the correlation functions of ultracold Rydberg plasma were calculated using Monte Carlo method for multicomponent plasma in the canonical ensemble in \([8]\). Radial distribution functions (RDF) were calculated.

It was discovered \([5]\) that with rising of the nonideality parameter (i.e. rising the density or lowering the temperature) the system structure undergoes a transformation from gas-like (RDF shows neither short nor long range order correlations) through liquid-like (short range order emerge) to solid-like periodic structure (long range order correlations in RDF). The diagrams representing the system structure properties for 36th level set of simulations are shown in figure 2.

The structure change may be due to the phase transition. But simulations accuracy for the model does not allow getting state equation exact enough to find the critical points and binodal lines. From the other hand (as one can see in figure 1) pseudopotentials can be approximated with some sort of a straight line for small distances and Coulomb law for big ones. That is how the “shelf Coulomb” model for ultracold Rydberg plasma emerges.

3. The “shelf Coulomb” model results
This model is defined by interaction pseudopotentials between charged particles of two kinds (electrons and ions) as follows:
\[
\beta \Phi_{ee}(x) = \beta \Phi_{ii}(x) = x^{-1},
\] (6)
\[
\beta \Phi_{ee}(x, \beta) = \begin{cases} 
-\varepsilon, & \text{if } x \leq \varepsilon^{-1}, \\
-x^{-1}, & \text{if } x > \varepsilon^{-1},
\end{cases}
\] (7)
Figure 1. Pseudopotentials. Discrete levels included in Slater sum from 10th: short dash line—1000 K; long dash line—100 K. Discrete levels included in sum from 36th: dot-dash line—10 K; double dot-dash line—5 K. Solid lines are actual pseudopotential and discontinuous lines are Coulomb potential reduced to given temperature.

where $x = r/\beta e^2$, $r$—distance between particles. In other words, a classical Coulomb potential is used as an interaction pseudopotential between like-charged particles, whereas “cut off” Coulomb

Figure 2. RDF Monte Carlo simulation points for system with discrete spectrum from 36th level: crosses—typical gas (ideal plasma) RDF; circles—liquid-like RDF; squares—solid-like crystal structure; solid line is the line where nonideality parameter is 1; dashed line—system is quantum, average interparticle distance becomes equal to electron de Broglie wavelength.
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 convenient to work in dimensionless variables in the model as follows: \( \gamma = \beta \varepsilon^2 n^{1/3} \) — nonideality parameter (\( n \)—particle density), \( v^* = 1/\gamma^3 \) — reduced specific volume, \( P^* = \beta P (\beta \varepsilon^2)^3 \) — reduced pressure, \( T^* = 1/\varepsilon \) — reduced temperature.

Classical Monte Carlo study has been carried out for the model and thermodynamic properties have been calculated [6,7]. Gas–liquid phase transition was discovered and the phase diagram, binodal, spinodal lines were obtained, the critical point was found: \( P^*_{\text{crit}} \approx 0.39 \), \( v^*_{\text{crit}} \approx 0.17 \) (\( \gamma_{\text{crit}} \approx 1.8 \)), \( T^*_{\text{crit}} \approx 1/13 \approx 0.076 \).

As one can see in figure 3 this model phase transition has rather low critical temperature (only one thirteenth of the potential depth \( \varepsilon \)). Important question is to extrapolate these results to actual Rydberg plasmas.

4. Compare “shelf Coulomb” and pseudopotential model results

The way to correlate the “shelf Coulomb” and the pseudopotential model results is to plot \( nT \) diagrams and the critical point data in the same parameter space.

One can easily find the depth of the pseudopotentials (figure 1) in \( kT \) units and convert the density from \( nT \) diagrams (figure 2) to specific volume. Next step is just to draw all these \( nT \) diagram points on the same space where the “shelf Coulomb” critical point is plotted (figure 3).

The result one may get is shown in figure 4. There is a good qualitative agreement, meaning there is a high chance this “model” phase transition phenomena exists in actual ultracold strongly coupled plasmas [10–13].

The possibility of experimental observation of such a phase transition is discussed in conclusion.

Figure 3. Critical point, binodal, spinodal lines for the “shelf Coulomb” model plasma.
5. Conclusion

Based on the “shelf Coulomb” critical parameters we may estimate the possibility of observing the gas–liquid phase transition in a real thermodynamically equilibrium plasma. It is necessary to take into account that for plasma of a specific chemical element (for example, hydrogen or cesium) the least possible value of the electron–ion pseudopotential corresponds to $\beta I$ (I is the atomic ionization potential). This choice of the pseudopotential depth determines the maximum possible plasma temperature corresponding to the transition to the two phase region.

This value is 12000 and 3500 K for hydrogen and cesium, respectively. I.e. the phase transition is possible for plasma of these elements when the plasma temperature is below these values. However, even at these temperatures the degree of ionization is so small that the critical point condition $\nu_{\text{crit}} = 1/\gamma^3 \approx 0.17$ yields a very high concentration of neutral particles. As a result, the conditions of applicability of the pseudopotential model, in which the mutual interaction of neutral particles and their interaction with charges are neglected, are violated. Additionally, high density of a neutral subsystem makes the diagnostics of a charged subsystem practically impossible.

These facts mean it is correct to say that the phase transition does not exist in equilibrium low temperature plasmas and the only known opportunity to find this “shelf Coulomb” model phase transition is to consider ultracold non-equilibrium Rydberg plasmas like plasma [10–13]. One should note that such plasmas are in partial thermodynamic equilibrium (in translational degrees of freedom) that exists only for a limited period of time.

This experimental work is currently being carried out in our group at Joint Institute for High Temperatures of Russian Academy of Sciences and approaches to diagnose the phase transition are being developed.
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