Thermodynamics and structure of a two-dimensional electrolyte by integral equation theory

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Monte Carlo simulations and integral equation theory were used to predict the thermodynamics and structure of a two-dimensional Coulomb fluid. We checked the possibility that integral equations reproduce Kosterlitz-Thouless and vapor-liquid phase transitions of the electrolyte and critical points. Integral equation theory results were compared to Monte Carlo data and the correctness of selected closure relations was assessed. Among selected closures hypernetted-chain approximation results matched computer simulation data best, but these equations unfortunately break down at temperatures well above the Kosterlitz-Thouless transition. The Kovalenko-Hirata closure produces results even at very low temperatures and densities, but no sign of phase transition was detected.

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I. INTRODUCTION

The properties of ionic fluids are strongly related to the systems dimensionality.¹ One-dimensional electrolytes always form an insulating system, whereas three-dimensional (3D) electrolytes are always conducting and have an infinite dielectric constant. Two-dimensional (2D) electrolytes are however special. The classical two-dimensional Coulomb fluid consists of equal number of logarithmically interacting positive and negative charges and serves as a physical model for systems whose important thermal excitations are vortices, examples being superconductive and superfluid thin films.² 2D ionic fluids have both the conducting and insulating phases, depending on the density of the electrolyte and the temperature. Such systems undergo a so called Kosterlitz-Thouless (KT)³ transition between an insulating and a conductive phase. At low temperatures the charges form neutral pairs or larger neutral clusters. As the temperature increases the pairs unbind and the system transitions into the conductive phase. The transition is accompanied by a universal jump in the dielectric response function.⁴ Evidence suggests^{5–8} that the Coulomb fluid undergoes also a vapor-liquid (VL) transition at finite densities and low temperatures. Even though the position and properties of both phase transitions have been studied extensively by theoretical methods^{9–11} as well as computer simulations,^{6,12,13} there is still some doubt regarding the position of the VL critical point and where exactly does the KT line terminate. Studies of a fluid of charged disks interacting via a logarithmic pair potential have also relevance for solutions of rigid cylindrical polyelectrolytes. Kholodenko and Beyerlin¹⁴ and Levin¹⁵ discuss the relation between the Manning counterion condensation¹⁶ and the Kosterlitz-Thouless phase transition.³

In addition to this study, there have also been reports of structural and thermodynamic properties of the 2D Coulomb fluid obtained using the integral equation theories (IET) in the

hypernetted chain (HNC) approximation.^{17,18} It was shown that the HNC approximation performs rather well in predicting both structural and thermodynamic properties at moderate temperatures and densities, while results deteriorate at low temperatures and densities due to a limited ability of the HNC to account for clustering. Its greater downfall is that the HNC equations break down at relatively high temperatures, making phase-transition studies rather difficult. Therefore, we set out to inspect whether any other closure relation manages to describe the Coulomb fluid as well as the HNC approximation does, and if they could be used to predict a phase transition. IET provides us with a fast and easy-to-implement method of calculating pair distribution functions and thermodynamic properties. IET also allows rather quick calculation of properties along the isotherms or isochores, but it also has drawbacks. It is based on approximations which can lead to convergence problems and even wrong results. Caution must therefore be exercised when using IET with a particular closure. In this work, beside using HNC, we tested also Kovalenko-Hirata (KH), mean spherical approximation (MSA), Rogers-Young (RY), and Zerah-Hansen (ZH)-like closures. We compared the IET results with results from computer simulations, and determined the no-solution region for each closure relation.

The paper is organized as follows. In Sec. II, we present the model with the interaction potential. In Sec. III, we write down integral equation theory details, in Sec. IV, we provide the details of Monte Carlo (MC) simulation. Results are presented and discussed in Sec V, where we provide a comparison of pair correlation functions and thermodynamics calculated from various IET approximations and those obtained from MC simulations.

II. THE MODEL

The system of 1:1 2D electrolyte was composed from N_+ particles with positive linear charge density q_+ and N_-

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particles having a negative linear charge density q_- . The interaction between two charged particles of diameter σ separated by distance r_{ij} is given by

$$u_{ij}(r_{ij}) = \begin{cases} -\frac{q_i q_j}{2\pi\epsilon\epsilon_o} \ln \frac{r_{ij}}{\sigma} & r_{ij} \geq \sigma \\ \infty & r_{ij} < \sigma, \end{cases} \quad (1)$$

where ϵ is permittivity of dielectric in which particles are embedded. The zero of the potential is chosen at contact of particles. If we use reduced units $r^* = \frac{r}{\sigma}$, $z_i = \frac{q_i L}{e_o}$, $u_{ij}^* = \frac{u_{ij}}{\lambda_B}$, where $\lambda_B = \frac{e_o^2}{2\pi\epsilon\epsilon_o L^2}$ and L is the characteristic length, Eq. (1) simplifies to

$$u_{ij}^*(r_{ij}^*) = \begin{cases} -z_i z_j \ln r_{ij}^* & r_{ij}^* \geq 1 \\ \infty & r_{ij}^* < 1. \end{cases} \quad (2)$$

III. THE INTEGRAL EQUATION THEORY

The basis of integral equation theory is the Ornstein-Zernike (OZ) equation¹⁹ which connects the total correlation function, $h(r)$, with the direct correlation function, $c(r)$. For a mixture the OZ relation reads as

$$h_{ij}(r_{12}) = \sum_l \rho_l \int d\mathbf{r}_3 c_{il}(r_{13}) h_{lj}(r_{32}), \quad (3)$$

One can improve upon the closure relation by mixing them with different relations to obey the consistency between the compressibility and virial pressure. For instance, the ZH closure introduced by Zerah and Hansen, interpolates between the HNC and the SMSA.²² We employed a similar closure, interpolating between the HNC and MSA closure:

$$c_{ij}(r) = \frac{\exp[f(r)(-\beta u_{ij}(r) + \gamma_{ij}(r))] - 1}{f(r)} - \gamma_{ij}(r), \quad (8)$$

where $f(r)$ is defined as

$$f(r) = 1 - \exp(-\alpha r).$$

The RY closure takes much the same route, mixing the Percus-Yevick closure with the HNC closure as²³

$$c_{ij}(r) = \exp(-\beta u_{ij}(r)) \frac{\exp[f(r)\gamma_{ij}(r)] - 1}{f(r)} - \gamma_{ij}(r) - 1. \quad (9)$$

In both cases parameter α is varied until thermodynamic consistency is achieved. The solution was deemed thermodynamically consistent, when the isothermal compressibilities calculated via the virial

$$\chi_v^{-1} = \left(\frac{\partial \beta P}{\partial \rho} \right)_{T, x_i}, \quad (10)$$

where ρ_l is the number density of species l . The total correlation function is related to the radial distribution function, $g_{ij}(r)$, through $g_{ij} = h_{ij} + 1$. A second relation between $h_{ij}(r)$ and $c_{ij}(r)$, called the closure relation, is needed in order to obtain a solution in integral equation theory. In general form this closure is written as

$$g_{ij}(r) = \exp(-\beta u_{ij}(r) + h_{ij}(r) - c_{ij}(r) + B_{ij}(r)), \quad (4)$$

where β is reverse temperature and $B_{ij}(r)$ an infinite sum of irreducible cluster diagrams called bridge graphs. Because the later is not known, we use different approximations. One of them is the HNC approximation²⁰ which neglects bridge graphs ($B_{ij}(r) = 0$) and has the following form:

$$c_{ij}(r) = \exp[-\beta u_{ij}(r) + \gamma_{ij}(r)] - 1 - \gamma_{ij}(r), \quad (5)$$

where γ_{ij} is $h_{ij} - c_{ij}$. HNC is particularly useful when particle interaction is long ranged as it is in the case of Coulomb fluid, but can sometimes overestimate the attraction between unlike-charged ions.²¹ We have also implemented the MSA and the KH closure,²⁴ known for its large convergence region. The MSA closure is written as

$$c_{ij}(r) = \begin{cases} -1 - \gamma_{ij}(r) & r < \sigma \\ -\beta u_{ij}(r) & r \geq \sigma, \end{cases} \quad (6)$$

while the KH closure takes the following form:

$$c_{ij}(r) = \begin{cases} \exp[-\beta u_{ij}(r) + \gamma_{ij}(r)] - \gamma_{ij}(r) - 1 & -\beta u_{ij}(r) + \gamma_{ij}(r) < 0 \\ -\beta u_{ij}(r) & -\beta u_{ij}(r) + \gamma_{ij}(r) \geq 0. \end{cases} \quad (7)$$

and compressibility route

$$\chi_c^{-1} = 1 - \lim_{k \rightarrow 0} \sum_{i,j} \sqrt{\rho_i \rho_j} \hat{c}_{ij}(k) \quad (11)$$

were in agreement. $\hat{c}_{ij}(k)$ is a 2D Fourier transform of the direct correlation function.

In order to solve equations obtained by combining the OZ relation with a selected closure relation, one must handle the long range behavior of the direct correlation function appropriately. We follow the path proposed in Ref. 18 and write the long range form of the pair potential and its transform as

$$u_{ij}^L(r) = -\frac{z_i z_j}{T} \left(\ln \left(\frac{r}{\sigma} \right) + \frac{1}{2} E_1 \left(\frac{r^2}{\sigma^2} \right) \right), \quad (12)$$

$$\tilde{u}_{ij}^L(k) = \frac{2\pi z_i z_j}{T(k\sigma)^2} \exp \left(-\frac{1}{4}(k\sigma)^2 \right), \quad (13)$$

where $E_1(x)$ is the exponential integral. We use this to define the following set of equations:

$$u_{ij}^S(r) = u_{ij}(r) - u_{ij}^L(r), \quad (14)$$

$$c_{ij}^S(r) = c_{ij}(r) + u_{ij}^L(r), \quad (15)$$

$$\gamma_{ij}^S(r) = \gamma_{ij}(r) - u_{ij}^L(r), \quad (16)$$

substitute them into Eqs. (3), (5)–(9), and solve the obtained expressions.

The computation were performed using 512 integration points and grid spacing in accordance with Lado.²⁵ We used Ng's scheme²⁶ to accelerate the iteration process. Once the radial distribution is acquired, different thermodynamic properties can be calculated. The internal energy for 1:1 electrolyte is obtained through

$$\frac{U^{ex}}{N} = \frac{1}{4}\pi\rho \sum_{i,j} \int_{\sigma}^{\infty} r u_{ij} g_{ij} dr, \quad (17)$$

where ρ is the total density. The virial pressure is given by

$$\frac{\beta P}{\rho} = 1 - \frac{\beta}{4} + \frac{\pi\rho\beta\sigma^2}{8} \sum_{i,j} g_{ij}(\sigma). \quad (18)$$

In order to see whether the integral equation theory can be used to correctly predict the KT transition we obtained the dielectric response function through

$$\epsilon_o^{-1} = \lim_{\mathbf{k} \rightarrow 0} \left(1 - \frac{2\pi\rho\beta}{k^2} \sum_{i,j} z_i z_j S_{ij}(k) \right), \quad (19)$$

where partial structural factors $S_{ij}(k)$ are related to the total correlation function via $S_{ij}(k) = x_i \delta_{ij} + x_i x_j \rho^* \hat{h}_{ij}(k)$, where x_i is the molar fraction of species i .²⁷

IV. MONTE CARLO SIMULATION DETAILS

To obtain thermodynamic and structural properties of the 2D Coulomb fluid we applied the Monte Carlo simulation method in the canonical (N,V,T) ensemble using periodic boundaries condition and minimum image. To avoid effects due to a finite size of the system the long range interactions were treated by the Ewald summation method.²⁸

Clusters start to form at lower temperatures. This makes single particle moves less efficient due to a large potential barrier preventing particles from leaving clusters. In order to increase the acceptance ratio we used cluster moves developed by Ferrenberg and Swendsen and modified by Wu *et al.*²⁹ alongside single particle moves. Here is a brief explanation of the used algorithm. Two ions are considered a part of the same cluster if they are oppositely charged and less than a cut off distance apart, which was set to 1.5σ in the present work. When a cluster is selected the whole cluster is randomly displaced. The move is accepted if it does not lead to an overlap or formation of a new cluster, and if the move is energetically favorable.

All simulations were performed with 102 particles, due to a considerable rise in computational costs at temperatures where the gas-liquid transition is expected. One hundred particles in 2D is equivalent to 1000 particles in 3D. We performed also simulation with 500 and 1000 particles to assure there were no size effects. The 10^6 moves per particle were needed to equilibrate the system. The statistics were gathered over the next 2×10^6 moves to obtain well converged results.

The dielectric response function was calculated by a slightly different form of Eq. (19),

$$\epsilon_o^{-1} = \lim_{\mathbf{k} \rightarrow 0} \left(1 - \frac{2\pi}{k^2 k_B T L^2} \langle q_{\mathbf{k}} q_{-\mathbf{k}} \rangle \right), \quad (20)$$

where $q_{\mathbf{k}} = \sum_i \exp(-i\mathbf{k} \cdot \mathbf{r}_i)$ and $\langle \rangle$ denotes an ensemble average. The limit in Eq. (20) was evaluated by averaging over the three lowest allowed wave vectors $\mathbf{k}$ in the periodic simulation cell as was previously done by Orkoulas and Panagiotopoulos.⁶ The pressure was calculated by virial equation (18). Heat capacities C_v were obtained from energy fluctuations,

$$C_v = \frac{\langle U^2 \rangle - \langle U \rangle^2}{k_B T^2}, \quad (21)$$

where $\langle U \rangle$ is the average internal energy of the system and $\langle U^2 \rangle$ the average square of internal energy.

V. RESULTS AND DISCUSSION

First we set out to inspect whether any of the five selected IET could be used to investigate the phase transitions characteristic for the 2D Coulomb fluid. In Figure 1, we have plotted convergence area depending on temperature and density of the system. Our results show that the HNC, MSA, RY, and ZH-like closure cannot be used to determine the KT transition line nor the VL curve for the following reasons: (i) the no-solution boundary of the HNC lies at temperatures higher than those of the KT and VL transition, (ii) use of the MSA closure leads to negative values for the pair distribution functions at transition temperatures, and (iii) one cannot obtain thermodynamically consistent solution with either of the mixed closure relations at transition temperatures. On the other hand, convergence was achieved even at very low temperatures and densities with the KH closure, so in principle it could be used to predict both transition lines and the position of the VL critical point.

Next we compare pair distribution functions obtained from IET with the results of MC simulations in Figures 2–5. The HNC approximation describes the 2D Coulomb fluid rather well at temperatures and densities away from the no-solution boundary, the agreement between the MC and HNC data being especially good in case of oppositely charged ions. The agreement deteriorates at lower densities, more visibly for like-charged ions pair distribution function. At high densities we can also see that HNC has problems predicting contact values for oppositely charged ions. The results obtained with the ZH-like closure lie between those obtained with the HNC and MSA closure, which is expected as the ZH-like closure interpolates between those two closures. In the range of temperatures where we were able to obtain results for both mixed closures, the ZH-like closure outperforms the RY closure at predicting the pair distribution function for like charged ions as well as for oppositely charged ions. At higher temperatures the ZH-like closure performs almost as well as the HNC, but the agreement with the MC data considerably worsens at lower temperatures and the pair distribution function behaves similarly to that obtained via the MSA closure. Among studied closure relations the MSA clearly performs the worst at

FIG. 1. Convergence regions for (a) HNC, (b) KH, (c) MSA, (d) ZH, and (e) RY closure. Convergence is above the line for HNC and KH. The numbers on the MSA part have the following meaning: 1, 3-convergence is achieved, but $g(r^*)$ hold negative values at certain values of r^* ; 2-method converges and gives positive values for $g(r^*)$; 4-method does not converge. In case of the ZH and RY closures, thermodynamical consistency is achieved in the region between the two lines.

all inspected conditions. At modest temperatures and densities the KH results for partial distribution functions for like charged ions agree with the simulation data, while those for oppositely charged ions do not. As density and temperature decrease the predictions of the KH for both pair distribution functions disagree with MC data.

Results for the excess internal energy and excess specific heat at constant volume for reduced temperatures 0.8

and 0.4 are presented in Figure 6. IET perform rather well at modest and high densities. The agreement is particularly good in case of the HNC closure. The ZH-like and RY closures also perform well, though the agreement with the MC energy data slightly worsens as the density increases. Among selected closures, the KH closure is clearly the worst at describing density dependence of U_{ex} and C_v^{ex} , predicting energies that are too high and specific heats that are too low.

FIG. 2. Pair distribution functions for (a) equally and (b) oppositely charged ions at $T^* = 0.8$ and $\rho^* = 0.15$. Circles correspond to MC results, pink solid line to HNC results, blue dashed line to KH results, orange dotted line to RY results, the red dashed-dotted line to ZH results, and the green long dashed line to MSA results.

FIG. 3. Same as Figure 2, but at $T^* = 0.8$ and $\rho^* = 0.48$.

FIG. 4. Same as Figure 2, but at $T^* = 0.6$ and $\rho^* = 0.15$.

FIG. 5. Same as Figure 2, but at $T^* = 0.4$ and $\rho^* = 0.02$.

At both studied temperature the use of IET leads to a maxima at lower densities in both the energy and specific heat. These are not reproduced by MC simulation results, which show a monotonic decrease of both thermodynamic quantities. The disagreement is especially big in the area where for-

mation of clusters is important and IET cannot handle this correctly.

In Figure 7, we show pressure results for two sets of reduced temperatures, $T^* = 0.8$ and $T^* = 0.4$. At reduced temperature 0.8 and reduced densities below 0.05, MC and IET

FIG. 6. Density dependence of (a) the excess energy per particle and (b) excess specific heat at constant volume at $T^* = 0.8$, (c) the excess energy and (d) heat capacity at $T^* = 0.4$. Circles correspond to MC results, pink solid line to HNC results, blue dashed line to KH results, orange dotted line to RY results, the red dashed-dotted line to ZH results, and the green long dashed line to MSA results. At $T^* = 0.4$ results could be obtained only for the HNC and KH closure.

FIG. 7. Density dependence of the pressure at (a) $T^* = 0.8$ and (b) $T^* = 0.4$. Circles correspond to MC results, pink solid line to HNC results, blue dashed line to KH results, orange dotted line to RY results, the red dashed-dotted line to ZH results, and the green long dashed line to MSA results.

results for pressure coincide, but as the density increases the results disagree more and more with HNC showing greatest disagreement. We can see that at $T^* = 0.4$, where only HNC and KH closure produce physically meaningful results, the disagreement with the MC data occurs at even lower reduced densities. The disagreement is again due to the inability of IET to take into account cluster formation.

Among selected closures only KH closure produces results in the region of temperatures and densities where the KT and VL transitions are expected. A sign of KT transition is a discontinuous jump of the dielectric response of the system from a finite value to zero as the transition temperature is approached from below. Figure 8 shows density and temperature dependence of the dielectric response function. We can see that integral equations fail to predict proper behavior. Not only do our results obtained using the KH closure show no sign of such a jump at KT transition densities, the dielectric response function increases with temperature. We carried out additional calculations, increasing the density while keeping the temperature constant. In this case we did observe a jump in the dielectric response function, but at temperatures where,

according to our MC simulations and results from other authors the system should be in the conductive phase at all densities. We also tried to determine the position of the VL transition by observing the density dependence of pressure in a range of reduced temperatures from 0.02 to 0.08. The pressure behaved monotonically at all inspected temperatures, showing no sign of phase transition.

VI. CONCLUSIONS

We have discussed the thermodynamics, structure, and possible phase transitions in 2D electrolyte, using Monte Carlo computer simulations and different variants of integral equation theories with various closures: HNC, MSA, KH, RY, and ZH. Among selected closures, the HNC closure shows the best agreement with simulation data, but it loses convergence in area of phase transition. Furthermore, we showed that only KH closure produces convergent and physically meaningful results in the region of KT and VL transition, but does not predict transition lines or the VL critical point.

FIG. 8. (a) Temperature dependence of the dielectric response function at $\rho^* = 0.01$. (b) Density dependence of the dielectric response function at $T^* = 0.8$. In both figures circles correspond to MC results and blue dashed lines to KH results.

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