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Surface Properties of the Three-Dimensional One-Component Plasma

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Extending earlier work by us Badiali *et al.* [*J. Phys. C: Solid State Phys.* **16**:2183 (1983)] we give further evidence for the usefulness of using spherical boundaries to calculate the bulk and surface properties of the three-dimensional one-component plasma (OCP) by Monte Carlo. Results are reported for the density profile of a "charged" OCP and for the pair distribution function parallel to the surface of an "open" system and of a neutral OCP near a hard wall. The charge fluctuations are calculated.

KEY WORDS: Coulomb systems; surface properties; density profile; correlations; Monte Carlo simulations.

1. INTRODUCTION

In a previous publication$^{(1)}$ (hereafter referred to as I) we have demonstrated that the surface density profile of the one-component plasma (OCP) in a neutralizing background can be obtained from Monte Carlo (MC) calculations by confining ions and background to a spherical volume. Both the situations where the ions are in contact with an impenetrable wall and where they are confined by the background itself have been considered. The appropriateness of using spherical boundaries was inferred from the independence of the results on the system size and the existence of a large central region inside which the properties of the system (e.g., internal energy or pair distribution function) were identical to those of a homoge-

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neous bulk system. Here we give further evidence for the suitability of using spherical boundaries by calculating the charge fluctuations in subregions of the system; in particular, it is shown that inside the central region of the system their behavior is that expected for a homogeneous bulk system.(2,3)

The main purpose of this paper is, however, to report MC simulation results for the ionic density profile near a hard wall in a "globally charged" OCP and the two-body correlation functions of particles located at equal distance from the surface. By "globally charged" OCP we mean a system in which the charge of the ions exceeds the total charge of the background by an amount which is proportional to the surface S of the system. (If Q_e is the excess charge we define σ by $Q_e = e\sigma S$).

Jancovici(4) has observed that, in the thermodynamic limit, a system with such an excess charge gives rise to the same surface layer structure as a system limited by a hard wall with a surface charge density $-e\sigma$. Although a rigorous proof of this result exists only for the two-dimensional OCP at the special value $\Gamma = \beta e^2 = 2$ of the coupling constant,(4) we expect it to be more generally valid for the two- and three-dimensional OCP at all couplings.

By varying the system size, keeping σ fixed, we show that for coupling constant $\Gamma = \beta e^2/a \lesssim 30$ [$\beta = 1/kT$ inverse temperature, $a = (4\pi\rho/3)^{-1/3}$, ρ density] about 600 particles are sufficient to produce density profiles close to their thermodynamic limit. These are compared with approximate theoretical predictions for the density profile near a charged *plane* hard wall.

The calculation of the pair distribution function (p.d.f.) parallel to the surface gives insight into the modification of the structure in the layers near the surface and permits evaluation of the validity of approximating this structure by that of an equivalent two- or three-dimensional bulk fluid.

Details of the MC computations are presented in Section 2, and the main conclusions are summarized in Section 3.

2. MONTE CARLO CALCULATIONS

We consider a system of N point ions ($N = 329$ and 679) of charge e enclosed in a spherical volume V of radius R_W the surface of which is impenetrable to the ions. A uniform background with density ρ_B and total charge opposite to the charge Ne of the ions occupies a concentric spherical volume of radius R_0. We shall deal with the following situations:

(1) $R_W = R_0$. This choice is appropriate for studying the surface properties of a neutral system near a hard wall.

(2) $R_W < R_0$. This choice has been made for studying the surface

properties of the ions in a charged OCP. Indeed, one immediately verifies that inside the volume of radius R_W there is an excess charge

$$Ne - \frac{4\pi}{e} \rho_B R_W^3 e = \frac{4\pi}{3} \rho_B \left(R_0^3 - R_W^3\right) e \tag{1}$$

which, as outlined in the Introduction, we believe to give rise to a surface structure identical to that near a uniformly charged hard wall with surface charge density:

$$-\sigma e = \frac{(4\pi/3)\left(R_0^3 - R_W^3\right)\rho_B e}{4\pi R_W^2} \tag{2}$$

For the 329-particle system we chose $R_W/R_0 = 0.95$ (excess charge of 15% of the total ionic charge). For the larger system ($N = 679$) R_W was chosen to give the same "surface charge" density as for the 329-particle system. The value of σ was kept fixed ($\sigma a^2 = 0.0868$) for all couplings considered ($\Gamma = 1, 10, 30$).

(3) $R_W \gg R_0$. This situation corresponds to an "open" system. The ions will be confined by the background itself. Note that the choice of a finite value for R_W (typically $R_W \sim 4R_0$ in our computations) is needed only in order to define unambiguously a thermodynamic limit (cf. I).

2.1. Pair Distribution Function Parallel to the Interface

We have calculated the p.d.f. $g_R(r)$ of two particles located between the distances R and $R + \Delta R$ of the center of the spherical volume comprising the system and separated by a distance $r = R\theta$, where θ is the angle between the vectors joining the center of the volume to the particle positions. The value of ΔR is $\sim 0.1a$. Two systems were considered: an "open" system at $\Gamma = 1$ and a neutral system near a hard wall at $\Gamma = 20$. The results are depicted in Figs. 1 and 2, respectively, together with the corresponding density profiles and the bulk p.d.f. $g_B(r)$. For the "open" system, $g_R(r)$ does not differ notably from the bulk p.d.f. when the value of R increases (at least within the statistical uncertainty of the computations). In particular, no qualitative change in the p.d.f. occurs when R becomes larger than R_0 (ions outside the background). Of course, long and expensive computations would be necessary in order to obtain accurate values for $g_R(r)$ in the region $R \gtrsim 1.5R_0$.

Concerning the neutral system at $\Gamma = 20$, there is an obvious qualitative variation of $g_R(r)$ according to which R corresponds to a large or small value of the local density. The first peak in $g_R(r)$ is more (less) pronounced than the corresponding peak in the bulk p.d.f. when the local density is

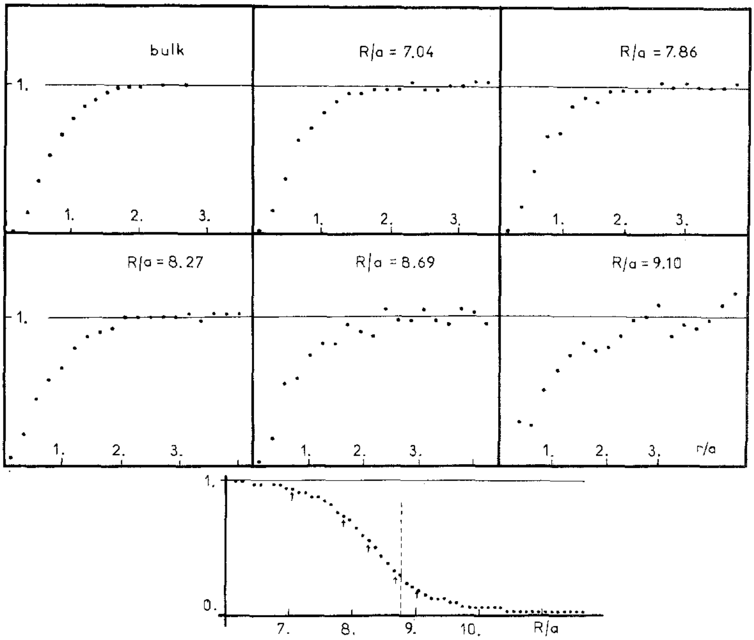

Fig. 1. Pair distribution function $g_R(r)$ for particles equally distant from the surface of an open system at $\Gamma = 1$. Are shown also the bulk p.d.f. and the density profile. The values of R for which $g_R(r)$ is shown are marked by arrows on the density profile. The distance R is measured from the center of the spherical volume. The boundary of the background is located at $R_0/a = 8.79$.

higher (lower) than the bulk density indicating the existence of a local order stronger (weaker) than in the bulk phase.

The results lead to the obvious conclusion that the assumption $g_R(r) \approx g_B(r)$ near the surface is certainly not valid for $\Gamma > 10$, and consequently, approximate theories for the density profile, based on this approximation, will be in error for $\Gamma > 10$ (cf. I).

A possible interpretation of the present results would be that, as noticed for uncharged systems,(5,6) $g_R(r)$ can be approximated, in the layer close to the wall and for $r/a \sim 1$, by the p.d.f. of a homogeneous two-dimensional OCP, with $1/r$ interaction, at the value of Γ calculated using the local value of the density. Unfortunately, not sufficiently detailed MC results are presently available for this two-dimensional OCP to verify this hypothesis. At all events, $g_R(r) - 1$ is likely to decrease, for large r, as $1/r^\nu$ (ν dimensionality)(7) in marked contrast with the decay of the bulk p.d.f. Obviously, in our case, statistical uncertainties and the use of a spherical geometry preclude evaluation of the asymptotic behavior of $g_R(r)$.

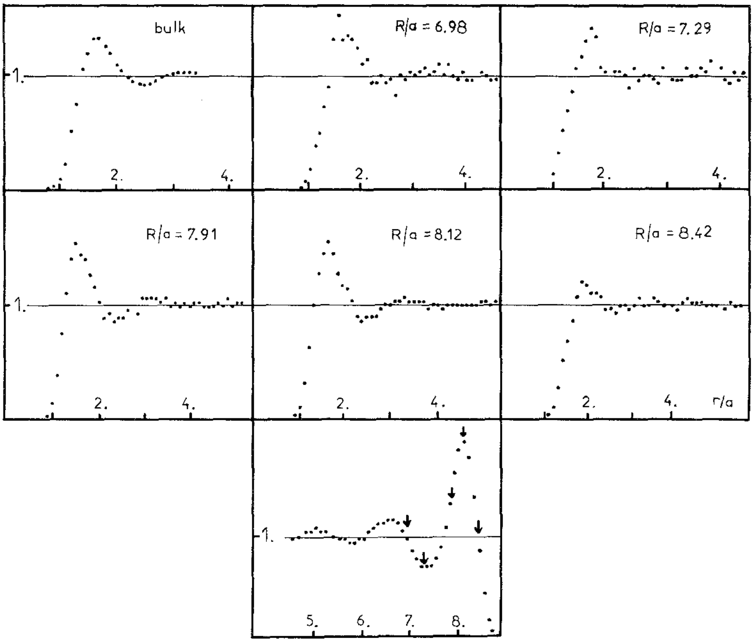

Fig. 2. Same as Fig. 1 but for a neutral OCP at $\Gamma = 20$ near a hard wall located at $R_W/a = 8.79$.

2.2. Density Profile near a Charged Hard Wall

Monte Carlo results for the density profile of a charged OCP are shown in Figs. 3–5 for $\Gamma = 1$, 10 and 30, respectively. At $\Gamma = 1$, comparison of the results for 329 and 679 particles shows that, if the excess charge is taken proportional to the surface, the density profile remains unchanged so that the thermodynamic limit seems already reached for the smaller system ($N = 329$). For the higher values of Γ considered, the 679-particle results are likely to be close to the thermodynamic limit. In that case we can legitimately compare the density profiles obtained from simulation with theoretical results pertinent to a OCP in contact with an infinite plane wall bearing a uniform charge density equal to $-\sigma e$.

The theoretical results we compare with (and which we shall denote HNC/MC) are derived from an exact equation, first proposed by Lovett *et al.*$^{(8)}$ and Wertheim$^{(9)}$ (see also Ref. 10), for the one-particle distribution function:

$$\nabla_r \log \rho(r) = \int d\mathbf{r}'\, c(\mathbf{r},\mathbf{r}')\, \nabla_{r'} \rho(r') \qquad (3)$$

in which the inhomogeneous two-body direct correlation function $c(\mathbf{r},\mathbf{r}')$ is

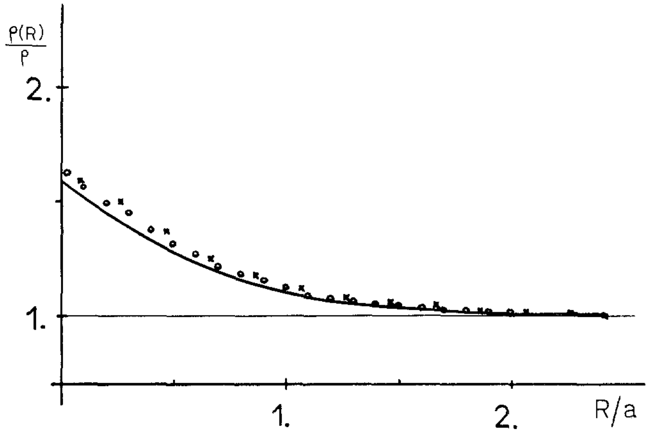

Fig. 3. Density profile of a charged OCP at $\Gamma = 1$ ($\sigma a^2 = 0.0868$). Open circles: MC for 679 particles; crosses: MC for 329 particles; solid line: theory (HNC/MC). The distance R is measured from the hard wall.

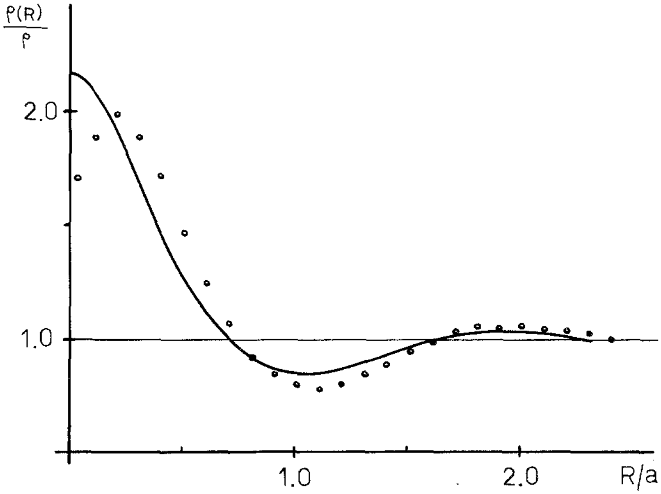

Fig. 4. Same as Fig. 3 but $\Gamma = 10$.

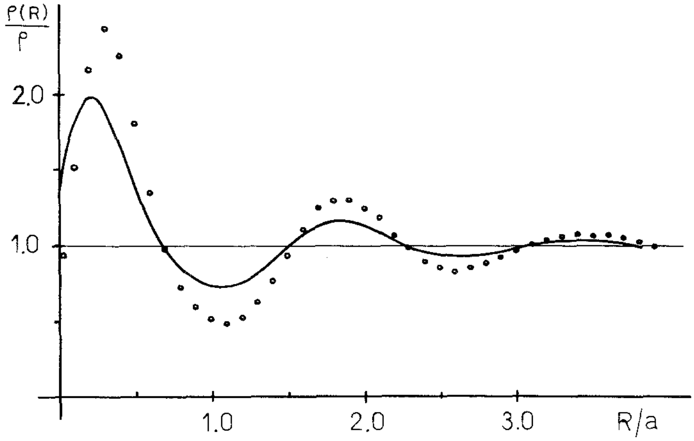

Fig. 5. Same as Fig. 3 but $\Gamma = 30$.

approximated by its bulk phase value $c_B(|\mathbf{r} - \mathbf{r}'|)$. The numerical solution of (3), using MC results(11) for $c_B(|r - r'|)$, follows exactly the lines given in I.

From Fig. 3 it appears that for $\Gamma = 1$, the density profile decays monotonically, MC and theoretical results are in quite good agreement, confirming the validity of approximating $g_R(r)$ by $g_B(r)$. For the higher couplings ($\Gamma = 10$ and 30) a layered structure is observed in the vicinity of the wall. Compared to the case of an uncharged wall (cf. I), the positions of the layers are notably shifted in the direction of the wall. The theoretical predictions reproduce the MC results only qualitatively.

2.3. Charge Fluctuations

In an equilibrium Coulomb system the mean square fluctuations $\langle Q^2 \rangle$ in the net electric charge Q inside a subregion is proportional to the surface area of this region.(2) Similarly, the joint charge fluctuations $\langle Q_{\Lambda_1} Q_{\Lambda_2} \rangle$ in adjacent regions Λ_1 and Λ_2 grow as their common surface area.(3)

We have verified these relations by calculating the mean square fluctuations $\langle Q^2 \rangle$ in concentric spheres and the joint charge fluctuations $\langle Q_{\Lambda_1} Q_{\Lambda_2} \rangle$ in adjacent concentric half-spheres of increasing radius R. Figure 6 shows $\langle Q^2 \rangle$ as a function of R^2 for an "open" system and for a globally charged system near a hard wall at $\Gamma = 1$. Up to $R/a \simeq 7$ which delimits the region inside which both systems are homogeneous (cf. density profiles on Figs. 1 and 3), the charge fluctuations are seen to vary linearly

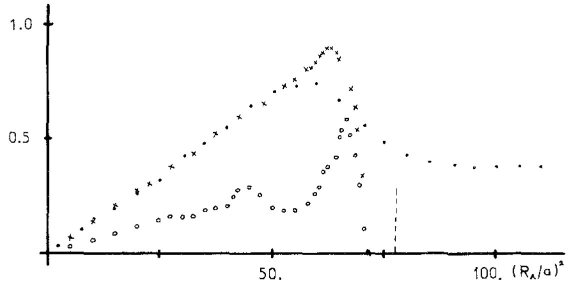

Fig. 6. Mean square fluctuations $\langle N_\Lambda^2 \rangle - \langle N_\Lambda \rangle^2 / N$ of the number of ions N_Λ contained in concentric spherical volumes of radius R plotted as a function of $(R/a)^2$ (N total number of ions in the system). Filled circles: "open" system at $\Gamma = 1$ $[(R_0/a)^2 = 77.3]$; crosses: charged OCP at $\Gamma = 1$; open circles: charged OCP at $\Gamma = 30$ $[(R_W/a)^2 = 71.4]$; $\sigma a^2 = 0.0868$.

with surface area $4\pi R^2$. The average value of $\langle Q^2 a^2 \rangle / 4\pi R^2 e^2$ is 0.073 ± 0.004 for an "open" system and 0.073 ± 0.003 for the charged system, in good agreement with the theoretical prediction for a homogeneous neutral bulk system:$^{(2,3)}$

$$\frac{Ka^2}{e^2} = -\frac{1}{4}\rho_B^2 a^2 \int d\mathbf{r}\, r \left[g_B(r) - 1 \right] = 0.071 \pm 0.002 \qquad (4)$$

where $g_B(r)$ is the p.d.f. of the bulk OCP. The linear variation of $\langle Q^2 \rangle$ with surface area should be satisfied approximately as soon as the diameter of the spheres are larger than the Debye length $[\lambda_D / a = 1/(3\Gamma)^{1/2}]$, which is in accord with our findings.

Beyond $R/a > 7$ the systems are inhomogeneous and no theoretical interpretation is available any more. In the "open" system, the charge fluctuations inside the particular volumes we consider appear to settle to a constant value for $R/a > 9.5$. In these regions the density profile decreases as $1/R^2$ (cf. I).

$\langle Q^2 \rangle$ has been further calculated for a charged system at $\Gamma = 30$ (cf. Fig. 6) and a neutral system near a hard wall at $\Gamma = 20$. In the regions of linear variation of $\langle Q^2 \rangle$ with surface area we find $\langle Q^2 \rangle a^2 / 4\pi R^2 e^2 =$ 0.031 ± 0.002 ($\Gamma = 30$) and 0.031 ± 0.002 ($\Gamma = 20$), respectively, in good agreement with the theoretical predictions for a bulk system 0.031 ± 0.002 ($\Gamma = 20$). Similarly, the joint charge fluctuations in adjacent half-spheres give $(\langle Q_{\Lambda_1} Q_{\Lambda_2} \rangle / \pi R^2)(a^2/e^2) = -0.031 \pm 0.004$ for the neutral system near a hard wall at $\Gamma = 20$.

These results again indicate that in the central region of our simulation sphere the system behaves as a bulk fluid, irrespective of the precise nature of the surface boundary ("open" system, charged, or neutral OCP near a hard wall).

3. CONCLUSION

From the results of I and those reported here it follows that the boundary conditions used (spherical volume limited by a hard wall) are valid for simulating the one-component plasma. They permit to study both the bulk and surface properties in a same computation. Clearly, owing to the screening property of the Coulomb interaction, this type of boundary conditions could equally well be applied for studying ionic solutions, in particular the double-layer problem, thus avoiding the use of Ewald sums or the computation of a self-consistent interaction for taking into account the long-range part of the Coulomb interactions.(12)

The density profiles computed for a "charged" system give strong indication that, in the thermodynamic limit, this system and a neutral system in contact with a uniformly charged hard wall are equivalent for a three-dimensional OCP.

Finally, the results obtained for the two-body distribution function $g_R(r)$ show that the correlations between particles at short distance $(r/a \sim 1)$ follow the variation of the local density and that, in order to obtain quantitative theoretical results for the density profile it is necessary to go beyond approximating the p.d.f. by its bulk value.

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