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Classical Coulomb Systems Near a Plane Wall. I

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The equilibrium structure of classical Coulomb systems bounded by a plane wall is studied near that wall. Several models are considered: the two-dimensional one-component plasma at a special value of the coupling constant (which makes the model exactly soluble), the two-dimensional and three-dimensional one-component and two-component plasmas in the weak-coupling limit (a Debye–Hückel type of approach is then used). Along a wall, the pair correlation functions decay only as an inverse power of the distance r, namely, as $r^{-\nu}$ for a ν-dimensional system ($\nu = 2, 3$). The one-body densities are also studied; the first BGY equation is used.

KEY WORDS: Coulomb systems; plasmas; surface properties; walls; correlations; density.

1. INTRODUCTION

In the equilibrium statistical mechanics of bulk Coulomb systems (plasmas), screening plays a central role. Although the Coulomb force is long-ranged, the correlations have a fast decay. This decay is believed to be exponential in many cases (see, e.g., Ref. 1), and such a behavior (Debye screening) has indeed been rigorously proved[(2)] for a classical weakly coupled system. For a classical two-dimensional one-component plasma, when the coupling constant has the special value $\Gamma = 2$, an explicit exact calculation is feasible,[(3,4)] and a still faster decay, a Gaussian one, is found.

In this paper, the equilibrium properties are studied near a plane wall. The behavior of a Coulomb system near a wall is of interest, for instance, for describing an electrolyte near a colloidal wall or near an electrode plate.

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In the present paper, the charges on the wall, if any, are considered as immobile (insulating wall). The pair correlation functions are computed for several classical models, and are shown not to behave in the same way as in the bulk system. In the direction parallel to the wall, the pair correlation functions are found to decay only as an inverse power of the distance r, namely, as $r^{-\nu}$ for a ν-dimensional system ($\nu = 2, 3$); a fast decay still occurs in any other direction. This slow decay can be qualitatively understood as a consequence of asymmetry effects. The screening cloud which surrounds a particle sitting near the wall is prevented by the wall from being spherically symmetrical, and the particle plus cloud system has a nonvanishing electrical dipole moment. This dipole moment cannot be assumed to be strongly localized, because a dipole moment creates far away an electrical field decaying only as an inverse power law, and this field would induce a remote charge distribution, in contradiction to the assumption of strong localization. Therefore, the pair correlation functions cannot have a fast decay in every direction.

Near a wall, the one-body densities are also of interest. The one-body densities are related to the pair correlation functions by the first equation of the Born–Green–Yvon (BGY) hierarchy. Here, this equation is used for determining the one-body densities near a wall for several models of weakly coupled plasmas.

We shall be interested in the structure of the plasma near an infinite plane wall, assuming that the state is invariant under translations parallel to the wall. Far from the wall, in the bulk plasma, the total charge density will be zero, but, in general, departures from neutrality will occur in the neighborhood of the wall. It is reasonable to expect that the equilibrium structure of the surface layer of the plasma will be determined by its net surface charge density but will not depend on the way in which this surface charge density has been attained. Consider for instance a slab of plasma between two distant parallel infinite plates A and B. If plate A is charged with a surface charge density σ and plate B with $-\sigma$, layers with surface charge densities $-\sigma$ and σ will be induced in the plasma near plates A and B, respectively. Another possible situation is that both plates are uncharged, but an appropriate excess of charged particles of one kind has been introduced in the plasma; they concentrate near the walls, and form layers with equal surface charge densities σ near each plate. In both situations, one should expect the layer with surface density σ near plate B to look exactly the same. The general expectation that the structure of a surface layer is determined by its net surface charge density will be vindicated in a special case in Section 2.

The models which are considered are, in succession, in Section 2 the two-dimensional one-component plasma with a coupling constant $\Gamma = 2$

(for which exact results can be obtained); in Section 3 the weakly coupled one-component plasma in two or three dimensions; and in Section 4 the weakly coupled symmetrical two-component plasma in two or three dimensions.

2. THE TWO-DIMENSIONAL ONE-COMPONENT PLASMA AT $\Gamma = 2$

2.1. The Model

The model is a system of N identical particles of charge e embedded in a uniform neutralizing background of opposite charge, in two dimensions. The Coulomb potential between two particles at a distance r from one another is, in two dimensions,

$$v(r) = -e^2 \ln(r/L)$$

where L is a length scale. The dimensionless coupling constant is $\Gamma = \beta e^2$, where $\beta = 1/k_B T$ (k_B is Boltzmann's constant and T is the temperature). At the special value $\Gamma = 2$, the equilibrium statistical mechanics of the model can be worked out exactly. The bulk properties[4,5] and the one-body density near a wall[6] have been previously studied. Here, the two-body density near a wall will be investigated, through the same approach, which will be briefly recalled.

We consider a system of N particles of charge e in a disk of radius R. The disk is filled with a background of uniform charge density $-e\rho$; ρ may be different from the particle number density $N/\pi R^2$, and therefore the system may carry a nonzero net charge. We define the length a by $\rho = 1/\pi a^2$. In the whole Section 2, we express all distances in units of a (in those units, $\rho = 1/\pi$). For the time being, the origin is at the center of the disk, and the position of the ith particle is $\mathbf{r}_i$. The potential energy is

$$V = V_0 + \frac{e^2}{2} \sum_{i=1}^{N} r_i^2 - e^2 \sum_{N \geq i > j \geq 1} \ln |\mathbf{r}_i - \mathbf{r}_j| \tag{2.1}$$

where V_0 is a constant; the second term in the right-hand side of (2.1) comes from the particle–background interaction. Each r_i is in the range $(0, R)$.

It is convenient to represent $\mathbf{r}_i$ by a complex number Z_i in the usual way: we set $Z_i = r_i \exp(i\theta_i)$, where (r_i, θ_i) are the polar coordinates of $\mathbf{r}_i$. When $\Gamma = e^2/k_B T = 2$, one obtains from (2.1) a Boltzmann factor

$$\exp(-V/k_B T) = A \exp\Big(-\sum_i |Z_i|^2\Big) \Big|\prod_{i>j} (Z_i - Z_j)\Big|^2 \tag{2.2}$$

where A is a constant. The product in (2.2) is a Vandermonde determinant

$$\prod_{i>j}(Z_i - Z_j) = \mathrm{Det}\begin{bmatrix} 1 & 1 & 1 & \cdots & 1 \\ Z_1 & Z_2 & Z_3 & \cdots & Z_N \\ Z_1^2 & Z_2^2 & Z_3^2 & \cdots & Z_N^2 \\ & & \cdots & & \\ Z_1^{N-1} & Z_2^{N-1} & Z_3^{N-1} & \cdots & Z_N^{N-1} \end{bmatrix} \tag{2.3}$$

which can be expanded as a sum of permutations:

$$\prod_{i>j}(Z_i - Z_j) = Z_1^0 Z_2^1 Z_3^2 \cdots Z_N^{N-1} + \cdots \tag{2.4}$$

The computation of the n-body density

$$\rho^{(n)}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n) = \frac{N!}{(N-n)!} \frac{\int \exp(-\beta V)\, d\mathbf{r}_{n+1} \cdots d\mathbf{r}_N}{\int \exp(-\beta V)\, d\mathbf{r}_1 \cdots d\mathbf{r}_N} \tag{2.5}$$

involves angular integrations which are easily performed, using (2.4) in (2.2) and the orthogonality property

$$\int_0^{2\pi} Z_i^p Z_i^{*q}\, d\theta_i = 2\pi\, \delta_{pq} r_i^{2p} \tag{2.6}$$

One is left with radial integrals which are incomplete gamma functions

$$\gamma(l+1, R^2) = \int_0^R \exp(-r^2) r^{2l} 2r\, dr = \int_0^{R^2} e^{-u} u^l\, du \tag{2.7}$$

One finds for the n-body density

$$\rho^{(n)}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n) = \rho^n \exp\left(-\sum_{i=1}^{n} |Z_i|^2\right) \mathrm{Det}\left[K(Z_i Z_j^*)\right]_{i,j=1,\ldots,n} \tag{2.8}$$

where

$$K(Z_i Z_j^*) = \sum_{l=0}^{N-1} \frac{(Z_i Z_j^*)^l}{\gamma(l+1, R^2)} \tag{2.9}$$

More explicit expressions for the one-body and two-body densities will now be obtained for semiinfinite systems bounded by different kinds of walls.

2.2. Plane Hard Wall

A plane hard wall is obtained from the circular wall of radius R which surrounds the disk by taking the limit $R \to \infty$. Since we want to allow for a possible net "surface" charge density $e\sigma$ along the wall, the number of particles must be

$$N = R^2 + 2\pi\sigma R \tag{2.10}$$

we expect the excess charge $2\pi e\sigma R$ to concentrate near the wall. The limit to be taken is $R \to \infty$, $N \to \infty$, while ρ and σ keep constant values. Since we want to study the structure near the wall, we take a new origin on the wall, and define the position of the ith particle by a shifted complex variable z_i such that

$$Z_i = -R + z_i \tag{2.11}$$

as $R \to \infty$, z_i is kept to a constant value. From the new origin on the wall, we draw an x axis normal to the wall (and directed towards the inside of the plasma) and a y axis along the wall; therefore z_i represents a vector of Cartesian components (x_i, y_i) drawn from the new origin, such that $z_i = x_i + iy_i$.

We want to compute the densities (2.8) in the above-described limit. In this limit, the dominant values of l in the sum (2.9) are close to R^2, and the incomplete gamma function can be replaced by an asymptotic form, which is valid for $l - R^2 = O(R)$, and which is obtained by writing the integrand of (2.7) as $\exp(-u + l\ln u)$ and expanding $-u + l\ln u$ around its maximum at $u = l$ up to the order $(u - l)^2$. One finds

$$\gamma(l+1, R^2) = \left(\frac{\pi}{2}\right)^{1/2} R\exp(-l + l\ln l)\left[1 + \Phi\left(\frac{R^2 - l}{R\sqrt{2}}\right) + O\left(\frac{1}{R}\right)\right] \tag{2.12}$$

where Φ is the error function

$$\Phi(t) = 2\pi^{-1/2}\int_0^t \exp(-u^2)\,du \tag{2.13}$$

Using (2.12) in (2.9), we obtain

$$\exp(-Z_iZ_j^*)K(Z_iZ_j^*) \sim \left(\frac{2}{\pi R^2}\right)^{1/2} \sum_{l=0}^{N-1} \frac{\exp(-Z_iZ_j^* + l\ln Z_iZ_j^* + l - l\ln l)}{1 + \Phi\left[(R^2 - l)/R\sqrt{2}\right]} \tag{2.14}$$

Expanding the argument of the exponential in (2.14) with respect to l around its maximum at $l = Z_iZ_j^*$ up to the order $(l - Z_iZ_j^*)^2$, replacing the sum upon l by an integral upon $t = (R^2 - l)/R\sqrt{2}$, and discarding terms of order $1/R$, one obtains, in the limit $R \to \infty$,

$$\exp(-Z_iZ_j^*)K(Z_iZ_j^*) = \frac{2}{\sqrt{\pi}}\int_{-\pi\sigma\sqrt{2}}^{\infty} \frac{\exp\left\{-\left[t - (z_i + z_j^*)/\sqrt{2}\,\right]^2\right\}}{1 + \Phi(t)}\,dt \tag{2.15}$$

Using (2.15) in (2.8), we obtain the one-body density

$$\rho^{(1)}(x) = \rho \frac{2}{\sqrt{\pi}} \int_{-\pi\sigma\sqrt{2}}^{\infty} \frac{\exp\left[-\left(t - x\sqrt{2}\right)^2\right]}{1 + \Phi(t)}\, dt \tag{2.16}$$

at a distance x from the wall, and the two-body density

$$\rho^{(2)}(z_1, z_2) = \rho^{(1)}(x_1)\rho^{(1)}(x_2) - \exp(-|z_1 - z_2|^2)|\rho^{(1)}[(z_1 + z_2^*)/2]|^2 \tag{2.17}$$

for two particles the positions of which are defined by $z_1 = x_1 + iy_1$ and $z_2 = x_2 + iy_2$.

The one-body density (2.16) has already been studied in Ref. 6. As expected, the excess charge in the plasma, if any, concentrates near the wall. The one-body density departs from its bulk value ρ only in a surface layer, the thickness of which is of the order of a, the average interparticle distance in the bulk.

The truncated two-body density is, from (2.17) and (2.16),

$$\begin{aligned} \rho_T^{(2)}(z_1, z_2) &= \rho^{(2)}(z_1, z_2) - \rho^{(1)}(x_1)\rho^{(1)}(x_2) \\ &= -\rho^2 \exp\left[-(x_1 - x_2)^2\right] \\ &\quad \times \left| \frac{2}{\sqrt{\pi}} \int_{-\pi\sigma\sqrt{2}}^{\infty} \frac{\exp\left\{-\left[t - (x_1 + x_2)/\sqrt{2}\,\right]^2 - it(y_1 - y_2)\sqrt{2}\right\}}{1 + \Phi(t)}\, dt \right|^2 \end{aligned} \tag{2.18}$$

If both particles are far away from the wall ($x_1, x_2 \gg 1$), the bulk expression[4]

$$\rho_T^{(2)}(z_1, z_2) = -\rho^2 \exp\left[-(x_1 - x_2)^2 - (y_1 - y_2)^2\right] \tag{2.19}$$

is recovered. Here, we are especially interested in the asymptotic behavior of (2.18) when particle 1 stays at a fixed position near the wall while particle 2 goes to infinity. If particle 2 recedes in any direction *not* parallel to the wall, $x_2 \to +\infty$ and (2.18) has a Gaussian-like decay; for instance, for a direction normal to the wall, the asymptotic behavior is given by (2.19). However, for a direction *parallel* to the wall, the asymptotic behavior is different; one must consider (2.18) as $y_1 - y_2 \to \pm\infty$, for fixed values of x_1 and x_2. Since the integral in (2.18) is the Fourier transform of a function of t which has a step discontinuity at $t = -\pi\sigma\sqrt{2}$, its asymptotic behavior as $y_1 - y_2 \to \pm\infty$ is governed by that discontinuity, and is readily obtained by integration by parts:

$$\int_{-\pi\sigma\sqrt{2}}^{\infty} \frac{\exp\left\{-\left[t-(x_1+x_2)/\sqrt{2}\,\right]^2 - it(y_1-y_2)\sqrt{2}\,\right\}}{1+\Phi(t)}\,dt$$

$$\sim \left.\frac{\exp\left\{-\left[t-(x_1+x_2)/\sqrt{2}\,\right]^2 - it(y_1-y_2)\sqrt{2}\,\right\}}{-i(y_1-y_2)\sqrt{2}\left[1+\Phi(t)\right]}\right|_{-\pi\sigma\sqrt{2}}^{\infty} \tag{2.20}$$

Using (2.20) in (2.18), we now find

$$\rho_T^{(2)}(z_1,z_2) \sim -\rho^2 \frac{2}{\pi} \frac{\exp\left\{-2\left[x_1^2+x_2^2+2\pi\sigma(x_1+x_2)+2\pi^2\sigma^2\right]\right\}}{\left[1+\Phi(-\pi\sigma\sqrt{2}\,)\right]^2}$$

$$\times \frac{1}{(y_1-y_2)^2} \tag{2.21}$$

Therefore, the correlations decay only as the inverse square distance in the direction parallel to the wall.

2.3. Charged Hard Wall

In Section 2.2, the surface charge density $e\sigma$ has been obtained by introducing an excess (or defect) of charged particles in the plasma. We show that the same surface layer structure can be obtained by charging a wall.

We now assume that the plasma lies *outside* a circle of radius R. This circle carries a "surface" charge density $-e\sigma$, i.e., its total charge is $-2\pi e\sigma R$. The plasma is made of N particles of charge e, in a background of charge density $-e\rho = -e/\pi a^2$; again we choose a as the unit of length ($a = 1$). The background is assumed at once to extend to infinity (this means that the background was first confined between two concentric circles of radii R and R', $R' > R$, and the limit $R' \to \infty$ has already been taken). The potential energy is

$$V = V_0 + e^2 \sum_{i=1}^{N} \left(\tfrac{1}{2} r_i^2 - \alpha \ln r_i\right) - \sum_{N \geqslant i > j \geqslant 1} \ln|\mathbf{r}_i - \mathbf{r}_j| \tag{2.22}$$

where

$$\alpha = R^2 - 2\pi\sigma R \tag{2.23}$$

Each r_i is in the range (R, ∞). When $\Gamma = e^2/k_B T = 2$, following the same steps as in Section 2.1, one finds again n-body densities of the form (2.8), where now

$$K(Z_iZ_j^*) = \sum_{l=0}^{N-1} \frac{(Z_iZ_j^*)^{l+\alpha}}{\Gamma(l+\alpha+1, R^2)} \tag{2.24}$$

Γ is the incomplete gamma function

$$\Gamma(l+\alpha+1, R^2) = \int_{R^2}^{\infty} e^{-u} u^{l+\alpha}\, du \tag{2.25}$$

As long as N is finite, we expect that the particles will occupy, outside the circle of radius R, an annular region of area N/ρ (cf. Section 2.4). In order to have this region extended to infinity, we take the limit $N \to \infty$. Now

$$K(Z_iZ_j^*) = \sum_{l=0}^{\infty} \frac{(Z_iZ_j^*)^{l+\alpha}}{\Gamma(l+\alpha+1, R^2)} \tag{2.26}$$

For studying the neighborhood of a plane charged hard wall, we set

$$Z_i = R + z_i \tag{2.27}$$

and take the limit of (2.26) as $R \to \infty$, for fixed values of α and z_i. The dominant values of $l+\alpha$ in (2.26) are close to R^2, and (2.25) can be replaced by its asymptotic form

$$\Gamma(l+\alpha+1, R^2) \sim \left(\frac{\pi}{2}\right)^{1/2} R \exp[-(l+\alpha) + (l+\alpha)\ln(l+\alpha)] \times \left[1 + \Phi\left(\frac{l+\alpha-R^2}{R\sqrt{2}}\right)\right] \tag{2.28}$$

The calculation goes on as in Section 2.2, and one obtains again (2.15) and the same n-body densities, with slowly decaying correlations in the direction parallel to the wall.

Therefore, the wall charged with a "surface" charge density $-e\sigma$ induces in the plasma a surface layer with a "surface" charge density $e\sigma$, identical to the one which has been studied in Section 2.2. This result confirms our expectation that the surface layer has a structure determined by its surface charge density, and does not depend on the way in which this surface density has been attained.

2.4. Soft Wall

A soft wall, which can also be studied exactly, is obtained by having the particles confined by the background itself. We consider again N particles in a circular background, and make at once the radius of the background infinite, for a fixed value of N. It will be shown that the particles gather in a circular region of area N/ρ, and the edge of this region will be studied, in the limit $N \to \infty$.

The potential energy is of the form (2.1), with each r_i now in the range $(0, \infty)$. The n-body densities are again given by (2.8), where now

$$K(Z_i Z_j^*) = \sum_{l=0}^{N-1} \frac{(Z_i Z_j^*)^l}{l!} \tag{2.29}$$

Since we expect the particle distribution to have a radius of the order of $\sqrt{N}$ and we want to study the edge of this distribution, we set

$$Z_i = -\sqrt{N} + z_i \tag{2.30}$$

and take the limit $N \to \infty$ in (2.29) for fixed values of z_i. Using Stirling's formula in (2.29), we obtain

$$\exp(-Z_i Z_j^*) K(Z_i Z_j^*) \sim \sum_{l=0}^{N-1} (2\pi l)^{-1/2} \exp(-Z_i Z_j^* + l \ln Z_i Z_j^* + l - l \ln l) \tag{2.31}$$

The calculation goes on as in Section 2.2; one obtains, in the limit $N \to \infty$,

$$\exp(-Z_i Z_j^*) K(Z_i Z_j^*) = \frac{1}{2}\left[1 + \Phi\left(\frac{z_i + z_j^*}{\sqrt{2}}\right)\right] \tag{2.32}$$

Using (2.32) in (2.8), one finds the one-body density[6]

$$\rho^{(1)}(x) = \rho \tfrac{1}{2}\left[1 + \Phi(x\sqrt{2})\right] \tag{2.33}$$

Thus, the background does behave like a soft wall. With our choice of coordinates, the distance x is measured from the plane on which the particle density has half its value in the bulk. On one side of this plane $(x > 0)$, the particle density quickly approaches the uniform value ρ which neutralizes the background; on the other side $(x < 0)$, the particle density falls to zero.

The truncated two-body density is now, from (2.17) and (2.33),

$$\rho_T^{(2)}(z_1, z_2) = -\rho^2 \exp(-|z_1 - z_2|^2) \frac{1}{4}\left|1 + \Phi\left(\frac{z_1 + z_2^*}{\sqrt{2}}\right)\right|^2 \tag{2.34}$$

Through a shift of the integration variable in the definition (2.13) of the function Φ, (2.34) can be rewritten as

$$\rho_T^{(2)}(z_1, z_2) = -\rho^2 \exp\left[-(x_1 - x_2)^2\right] \times \left|\frac{1}{\sqrt{\pi}} \int_{-\infty}^{(x_1 + x_2)/\sqrt{2}} \exp\left[-t^2 - it(y_1 - y_2)\sqrt{2}\,\right] dt\right|^2 \tag{2.35}$$

The asymptotic behavior of (2.35) when particle 2 goes to infinity is similar to the one which was studied in Section 2.2. If particle 2 recedes in any direction not parallel to the wall, $x_2 \to \pm\infty$, and (2.35) has a Gaussian-like decay. However, for a direction parallel to the wall, the asymptotic behavior of (2.35), obtained by integration by parts, is

$$\rho_T^{(2)}(z_1, z_2) \sim -\rho^2 \frac{\exp\left[-2\left(x_1^2 + x_2^2\right)\right]}{2\pi(y_1 - y_2)^2} \tag{2.36}$$

this is again a decay rate which goes only as the inverse square distance.

Finally, let us remark that the soft wall which has just been studied can be considered as a limiting case of a hard wall, when the surface layer of the plasma carries a "surface" charge density $e\sigma$ and $\sigma \to -\infty$. In this limit, there is an infinitely large defect of particles near the wall, and the edge of the particle distribution must be at an infinitely large distance $|\sigma|/\rho = \pi|\sigma|$ from the hard wall; the particles "feel" only the background, and no longer the hard wall. Indeed, in the limit $\sigma \to -\infty$, $\Phi(t)$ can be replaced by 1 in (2.15), which becomes, through a shift of the integration variable,

$$\exp(-Z_i Z_j^*)K(Z_i Z_j^*) \sim \frac{1}{2}\left[1 + \Phi\left(\frac{z_i + z_j^* + 2\pi\sigma}{\sqrt{2}}\right)\right] \tag{2.37}$$

in this way, we do recover the expression (2.32) appropriate to a soft wall, with, however, a shift of the origin (the midpoint of the soft wall is now at a distance $\pi|\sigma|$ of the original hard wall, as it should be).

2.5. The Screening Cloud near a Wall

The perfect-screening sum rule is well known in bulk Coulomb systems: a particle of charge e surrounds itself with a screening cloud the average charge of which is exactly $-e$. In the present model, it can be shown that this is also valid near a wall. The sum rule is

$$\int \rho_T^{(2)}(\mathbf{r}_1, \mathbf{r}_2)\, d\mathbf{r}_2 = -\rho^{(1)}(\mathbf{r}_1) \tag{2.38}$$

It holds for the hard-wall case of Sections 2.2 and 2.3 as well as for the soft-wall case of Section 2.4. The derivation of (2.38) is a straightforward calculation using the integral representations of $\rho^{(2)}$ and $\rho^{(1)}$.

In the bulk, the screening cloud is spherically symmetrical. Near a wall, it is not, and the particle plus cloud system has an electrical dipole moment $\mathbf{p}$ in the direction normal to the wall; it was explained in the Introduction how this dipole moment prevents the truncated two-body density from having a fast decay in every direction. For a particle at a position $\mathbf{r}_1$, the value of the dipole moment along the x axis is

$$p = \frac{e}{\rho^{(1)}(x_1)} \int (x_2 - x_1)\rho_T^{(2)}(\mathbf{r}_1, \mathbf{r}_2)\, d\mathbf{r}_2 \tag{2.39}$$

The integral in (2.39) can be calculated with the use of the integral representations of $\rho_T^{(2)}$; the results are

$$\int (x_2 - x_1)\rho_T^{(2)}(\mathbf{r}_1, \mathbf{r}_2)\, d\mathbf{r}_2 = -\frac{\exp\left[-2(x_1 + \pi\sigma)^2\right]}{(2\pi^3)^{1/2}\left[1 + \Phi(-\pi\sigma\sqrt{2})\right]} \tag{2.40}$$

for the hard-wall case, and

$$\int (x_2 - x_1)\rho_T^{(2)}(\mathbf{r}_1, \mathbf{r}_2)\, d\mathbf{r}_2 = -(8\pi^3)^{-1/2}\exp(-2x_1^2) \tag{2.41}$$

for the soft-wall case.

3. THE WEAKLY COUPLED ONE-COMPONENT PLASMA

3.1. The Pair Correlation Function near an Uncharged Hard Wall

In bulk Coulomb systems, the best-known way of computing pair correlation functions is the linearized Debye–Hückel approximation. This approach is believed to provide the leading term in an expansion with respect to the coupling constant, and thus it gives correct results in the weak-coupling limit.

For studying the correlations of a weakly coupled plasma near a wall, it is therefore a very natural idea to extend the Debye–Hückel method. This is what will be done in this section, for the simplest Coulomb system, i.e., the one-component plasma. Both the three-dimensional and two-dimensional cases will be treated.

We consider a ν-dimensional one-component plasma ($\nu = 2, 3$) confined in the half-space $x > 0$. The plane $x = 0$ is an uncharged hard wall, which contains the origin. A vector $\mathbf{r}$ is defined by its components $(x, \mathbf{y})$, where $\mathbf{y}$ is the set of the $\nu - 1$ components parallel to the wall. The interaction between two particles at a distance r from one another is

$$\begin{aligned} v(r) &= -e^2 \ln(r/L) \qquad (\nu = 2) \\ v(r) &= e^2/r \qquad\qquad (\nu = 3) \end{aligned} \tag{3.1}$$

The half-space $x > 0$ is filled with a uniform background the charge density of which is $-e\rho$, and particles of charge e the bulk density of which is ρ.

The pair-correlation function h is defined from the one-body and two-body densities by

$$\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2)-\rho^{(1)}(\mathbf{r}_1)\rho^{(1)}(\mathbf{r}_2)=\rho_T^{(2)}(\mathbf{r}_1,\mathbf{r}_2)=\rho^{(1)}(\mathbf{r}_1)\rho^{(1)}(\mathbf{r}_2)h(\mathbf{r}_1,\mathbf{r}_2) \quad (3.2)$$

The direct correlation function c is defined from h by the Ornstein–Zernicke relation

$$h(\mathbf{r}_1,\mathbf{r}_2)=c(\mathbf{r}_1,\mathbf{r}_2)+\int h(\mathbf{r}_1,\mathbf{r}_3)\rho^{(1)}(\mathbf{r}_3)c(\mathbf{r}_3,\mathbf{r}_2)\,d\mathbf{r}_3 \quad (3.3)$$

We now come to the linearized Debye–Hückel approximation.

Near the wall, the one-particle density $\rho^{(1)}(x)$ is distorted and differs from its bulk value ρ. However, since we are studying a weakly coupled system, we may use a successive approximation scheme. In zeroth-order approximation, $\rho(x)$ is the step function, $\rho^{(1)}(x)=0$ if $x<0$, $\rho^{(1)}(x)=\rho$ if $x>0$; this zeroth-order $\rho(x)$ will be used for computing the pair-correlation function. Then, in Section 3.2, this pair-correlation function will be used in the first equation of the BGY hierarchy for computing a more accurate one-particle density.

A simple way to obtain the Debye–Hückel approximation is to take in (3.3) for the direct correlation function the approximate form

$$c(\mathbf{r}_1,\mathbf{r}_2)=-\beta v(|\mathbf{r}_2-\mathbf{r}_1|) \quad (3.4)$$

Thus, the pair-correlation function h obeys the equation

$$h(\mathbf{r}_1,\mathbf{r}_2)=-\beta v(|\mathbf{r}_2-\mathbf{r}_1|)-\beta\rho\int_{x_3>0}h(\mathbf{r}_1,\mathbf{r}_3)v(|\mathbf{r}_2-\mathbf{r}_3|)\,d\mathbf{r}_3 \quad (3.5)$$

Another, equivalent, derivation of (3.5) is based on the linear-response theory: $\rho h(\mathbf{r}_1,\mathbf{r}_2)$ is the change in density at $\mathbf{r}_2$ when a particle is added at $\mathbf{r}_1$, and (3.5) states that this change in density is the linear response to both the potential created by the particle at $\mathbf{r}_1$ and the potential created by the particle distribution ρh itself.

The integral equation (3.5) can be transformed into a pair of partial differential equations. Note that h is also defined for $x_2<0$ by (3.5) itself. Taking the Laplacian Δ_2 with respect to $\mathbf{r}_2$ in both sides of (3.5), one obtains

$$(\Delta_2-\kappa^2)\left[\rho h(\mathbf{r}_1,\mathbf{r}_2)\right]=\kappa^2\delta(\mathbf{r}_2-\mathbf{r}_1) \qquad (x_1,x_2>0) \quad (3.6)$$

$$\Delta_2\left[\rho h(\mathbf{r}_1,\mathbf{r}_2)\right]=0 \qquad (x_1>0,\,x_2<0) \quad (3.7)$$

where

$$\kappa=\left[2(\nu-1)\pi\beta e^2\rho\right]^{1/2} \quad (3.8)$$

(κ^{-1} is the Debye length).[1,9] Equation (3.6) is just the familiar linearized Poisson–Boltzmann equation in the plasma, while (3.7) is the Poisson equation in the vacuum. These equations must be solved with the conditions that h and $\partial h/\partial x_2$ are continuous on the plane $x_2=0$ (since h is proportional to the electrostatic potential). One reduces the problem to a one-dimensional one by using the Fourier transform on the y coordinates

$$\hat{h}(x_1,x_2,l) = \int \exp[i\mathbf{l}\cdot(\mathbf{y}_2-\mathbf{y}_1)]h(\mathbf{r}_1,\mathbf{r}_2)\,d\mathbf{y}_2 \tag{3.9}$$

In terms of this transform, (3.6) and (3.7) become

$$\left(\frac{d^2}{dx_2^2}-\kappa^2-l^2\right)\left[\rho\hat{h}(x_1,x_2,l)\right] = \kappa^2\delta(x_2-x_1) \qquad (x_1,x_2>0) \tag{3.10}$$

$$\left(\frac{d^2}{dx_2^2}-l^2\right)\left[\rho\hat{h}(x_1,x_2,l)\right] = 0 \qquad (x_1>0,\, x_2<0) \tag{3.11}$$

The solution of (3.10) and (3.11), with the conditions that $\hat{h}$ and $d\hat{h}/dx_2$ are continuous at $x_2=0$ and that $\hat{h}\to 0$ as $x_2\to\pm\infty$, is easily found to be

$$\begin{aligned}\rho\hat{h}(x_1,x_2,l) = &-\frac{\kappa^2}{2(\kappa^2+l^2)^{1/2}}\\ &\times\left\{\exp\left[-(\kappa^2+l^2)^{1/2}|x_2-x_1|\right]+\frac{(\kappa^2+l^2)^{1/2}-l}{(\kappa^2+l^2)^{1/2}+l}\right.\\ &\left.\exp\left[-(\kappa^2+l^2)^{1/2}(x_1+x_2)\right]\right\} \qquad (x_1,x_2\geqslant 0)\end{aligned} \tag{3.12}$$

$$\rho\hat{h}(x_1,x_2,l) = -\frac{\kappa^2}{(\kappa^2+l^2)^{1/2}+l}\exp\left[-(\kappa^2+l^2)^{1/2}x_1+lx_2\right] \qquad (x_1\geqslant 0,\, x_2\leqslant 0) \tag{3.13}$$

where $l=|\mathbf{l}|\geqslant 0$. The pair correlation function in coordinate space is the Fourier transform inverse of (3.9)

$$h(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{(2\pi)^{\nu-1}}\int \exp[-i\mathbf{l}\cdot(\mathbf{y}_2-\mathbf{y}_1)]\hat{h}(x_1,x_2,l)\,d\mathbf{l} \tag{3.14}$$

where $\hat{h}$ is given by (3.12); we do not perform this transform explicitly.

It may be noted that, if we use (3.13) in (3.14), the quantity $h(\mathbf{r}_1,\mathbf{r}_2)$ which is obtained does have a physical meaning: one sees from (3.5) that $-(\beta e)^{-1}h(\mathbf{r}_2,\mathbf{r}_1)$ is the average electrostatic potential at a point $\mathbf{r}_2$ outside the plasma ($x_2<0$), knowing that there is a plasma particle at $\mathbf{r}_1$ ($x_1>0$).

The asymptotic behavior of the pair correlation function $h(\mathbf{r}_1,\mathbf{r}_2)$, when particle 2 goes to infinity, is easily obtained from (3.12) and (3.14). If particle 2 recedes in any direction not parallel to the wall, $x_2\to+\infty$, and h

decays exponentially. However, if particle 2 recedes in a direction parallel to the wall, one must consider the asymptotic behavior of (3.14) as $|\mathbf{y}_2 - \mathbf{y}_1| \to \infty$, for fixed values of x_1 and x_2; this behavior is governed by the kink of (3.12) at $\mathbf{l} = 0$ and is (see, e.g., Ref. 7)

$$\rho h(\mathbf{r}_1, \mathbf{r}_2) \sim -\frac{\exp[-\kappa(x_1 + x_2)]}{(\nu - 1)\pi|\mathbf{y}_2 - \mathbf{y}_1|^\nu} \tag{3.15}$$

Therefore, in the direction parallel to the wall, the correlations decay only as the inverse square ($\nu = 2$) or the inverse cube ($\nu = 3$) of the distance.

From (3.9) and (3.12), one sees that the perfect-screening sum rule is satisfied:

$$\rho \int_{x_2 > 0} h(\mathbf{r}_1, \mathbf{r}_2)\, d\mathbf{r}_2 = -1 \tag{3.16}$$

The screening cloud, however, has a dipole moment which is

$$e\rho \int_{x_2 > 0} h(\mathbf{r}_1, \mathbf{r}_2)(x_2 - x_1)\, d\mathbf{r}_2 = -e\kappa^{-1}\exp(-\kappa x_1) \tag{3.17}$$

3.2. The One-Particle Density near an Uncharged Hard Wall

We now come back to the one-particle density $\rho^{(1)}$ and compute it, using the approximate pair correlation function of Section 3.1 in the first equation of the BGY hierarchy. Let

$$e\mathbf{F}(\mathbf{r}_1 - \mathbf{r}_2) = e\frac{\mathbf{r}_1 - \mathbf{r}_2}{|\mathbf{r}_1 - \mathbf{r}_2|^\nu} \tag{3.18}$$

be the electrical field created at $\mathbf{r}_1$ by a particle located at $\mathbf{r}_2$. The average electrical field at $\mathbf{r}_1$ is

$$\mathbf{E}(x_1) = e\int_{x_2 > 0} \mathbf{F}(\mathbf{r}_1 - \mathbf{r}_2)\left[\rho^{(1)}(x_2) - \rho\right] d\mathbf{r}_2 \tag{3.19}$$

The first equation of the BGY hierarchy may be written as

$$\nabla\rho^{(1)}(x_1) = \beta e\mathbf{E}(x_1)\rho^{(1)}(x_1) + \beta e^2 \int_{x_2 > 0} \mathbf{F}(\mathbf{r}_1 - \mathbf{r}_2)\rho_T^{(2)}(\mathbf{r}_1, \mathbf{r}_2)\, d\mathbf{r}_2 \tag{3.20}$$

where $\rho_T^{(2)}$ is related to h by (3.2). In the weak-coupling limit, both $\rho^{(1)} - \rho$ and h are small quantities, and it is permissible to linearize (3.20) with respect to these quantities; one obtains

$$\nabla\rho^{(1)}(x_1) = \beta e\rho\mathbf{E}(x_1) + \beta e^2\rho^2 \int_{x_2 > 0} \mathbf{F}(\mathbf{r}_1 - \mathbf{r}_2)h(\mathbf{r}_1, \mathbf{r}_2)\, d\mathbf{r}_2 \tag{3.21}$$

The electrical field (3.19) is along the x axis; after the integration upon $\mathbf{y}_2$ has been performed, the x component becomes

$$E_x(x_1) = (\nu - 1)\pi e\left\{\int_0^{x_1}[\rho(x_2) - \rho]\, dx_2 - \int_{x_2}^{\infty}[\rho(x_2) - \rho]\, dx_2\right\} \tag{3.22}$$

The last term of (3.21) is also along the x axis, and it can be computed using the Fourier transform of F_x (the x component of **F**) with respect to **y**

$$\hat{F}(x,l) = \int \exp(i\mathbf{l}\cdot\mathbf{y})F_x(\mathbf{r})\,d\mathbf{y} = \frac{(\nu-1)\pi x}{|x|}\exp(-l|x|) \qquad (3.23)$$

and $\hat{h}(x_1,x_2,l)$ given by (3.12):

$$\begin{aligned} f(x_1) &= \beta e^2\rho^2\int_{x_2>0} F_x(\mathbf{r}_1-\mathbf{r}_2)h(\mathbf{r}_1,\mathbf{r}_2)\,d\mathbf{r}_2 \\ &= \frac{\beta e^2\rho^2}{(2\pi)^{\nu-1}}\int_{x_2>0}\hat{F}(x_1-x_2,l)\hat{h}(x_1,x_2,l)\,d\mathbf{l}\,dx_2 \\ &= \frac{\kappa^4}{(\nu-1)2\pi}\int_0^\infty \frac{\exp\left[-2x_1(\kappa^2+l^2)^{1/2}\right]}{\left[(\kappa^2+l^2)^{1/2}+l\right]^2}\,l^{\nu-2}\,dl \end{aligned} \qquad (3.24)$$

Therefore, Eq. (3.21) can be rewritten as

$$\frac{d}{dx}\left[\rho^{(1)}(x)-\rho\right]-\frac{\kappa^2}{2}\left\{\int_0^x\left[\rho^{(1)}(x')-\rho\right]dx'-\int_x^\infty\left[\rho^{(1)}(x')-\rho\right]dx'\right\} = f(x) \qquad (3.25)$$

where $f(x)$ is given by (3.24).

Equation (3.25) must be solved with the boundary condition that $\rho^{(1)}(x)-\rho\to 0$ as $x\to+\infty$. If $f(x)$ were a simple exponential $\exp(-px)$, the solution would be found as a combination of $\exp(-\kappa x)$ and $\exp(-px)$, namely,

$$\rho^{(1)}(x)-\rho = \frac{\kappa\exp(-\kappa x)-p\exp(-px)}{p^2-\kappa^2} \qquad (3.26)$$

The actual $f(x)$ is a superposition of exponentials, and the solution is the corresponding superposition of terms of the form (3.26):

$$\rho^{(1)}(x)-\rho = \frac{\kappa^4}{(\nu-1)2\pi} \times\int_0^\infty \frac{\kappa\exp(-\kappa x)-2(\kappa^2+l^2)^{1/2}\exp\left[-2x(\kappa^2+l^2)^{1/2}\right]}{\left[(\kappa^2+l^2)^{1/2}+l\right]^2(3\kappa^2+4l^2)}\,l^{\nu-2}\,dl \qquad (3.27)$$

The integral (3.27) can be numerically computed as a function of x. The resulting density profiles are shown in Fig. 1, for both the two-dimensional and the three-dimensional cases. There is an oscillation in $\rho^{(1)}(x)-\rho$, and the total surface charge density is easily shown to be zero,

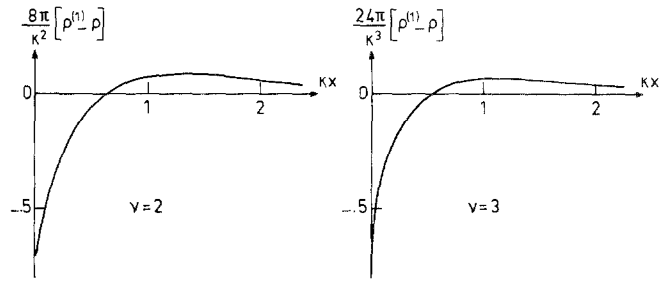

Fig. 1. The one-body densities for a weakly coupled one-component plasma, in two ($\nu = 2$) or three ($\nu = 3$) dimensions, near an uncharged hard wall.

as expected along an uncharged wall:

$$\int_0^{\infty} \left[\rho^{(1)}(x) - \rho\right] dx = 0 \tag{3.28}$$

When $x \to +\infty$, $\rho^{(1)}(x) - \rho$ decays exponentially as $\exp(-\kappa x)$.

The density at the wall is of special interest, since it is related to the "kinetic pressure" which differs from the usual "thermal pressure" for a one-component plasma.[10,11] At $x = 0$, the integral (3.27) can be performed analytically, with the results

$$\begin{aligned} \rho^{(1)}(0) - \rho &= -\left(\ln 3 - 1 + \frac{\pi\sqrt{3}}{9}\right)\frac{\kappa^2}{8\pi} = -0.703\,\frac{\beta e^2 \rho}{4} \qquad (\nu = 2) \\ \rho^{(1)}(0) - \rho &= -\frac{1 - 3\ln 3 + \pi\sqrt{3}}{4}\,\frac{\kappa^3}{24\pi} = -\frac{0.786\kappa^3}{24\pi} \qquad (\nu = 3) \end{aligned} \tag{3.29}$$

The corresponding kinetic pressures are

$$p^{(k)} = k_B T \rho^{(1)}(0) = \rho\left(k_B T - 0.703\,\frac{e^2}{4}\right) \qquad (\nu = 2) \tag{3.30a}$$

$$p^{(k)} = k_B T \rho^{(1)}(0) = \left(\rho - 0.786\,\frac{\kappa^3}{24\pi}\right) k_B T \qquad (\nu = 3) \tag{3.30b}$$

while the thermal pressures are[1,2]

$$p^{(\theta)} = \rho\left(k_B T - \frac{e^2}{4}\right) \qquad (\nu = 2) \tag{3.31a}$$

$$p^{(\theta)} = \left(\rho - \frac{\kappa^3}{24\pi}\right) k_B T \qquad (\nu = 3) \tag{3.31b}$$

For the two-dimensional system, (3.31a) is valid for all couplings, while (3.30a) is only the weak-coupling limit; however the value of $p^{(k)}$ at $\beta e^2 = 2$

is also known[6] and is $\rho k_B T \ln 2$. For the three-dimensional system, both (3.30b) and (3.31b) are weak-coupling limits. It can be checked that the sum rule of Choquard et al.,[11]

$$p^{(k)} - p^{(\theta)} = (\nu - 1)2\pi e^2 \rho \int_0^\infty \left[\rho^{(1)}(x) - \rho\right] x\, dx \tag{3.32}$$

is satisfied by our expressions.

3.3. Weakly Charged Hard Wall

If the hard wall carries a weak surface charge density $-e\sigma$, it is possible to compute the one-body density up to the first order in σ. The plasma is still assumed to be weakly coupled.

The one-body density $\rho^{(1)}$ is a function of σ, and it obeys the sum rule[13]

$$\frac{\partial \rho^{(1)}(x_1)}{\partial \sigma} = -2(\nu - 1)\pi\beta e^2 \int_{x_2 > 0} \rho_T^{(2)}(\mathbf{r}_1, \mathbf{r}_2)(x_2 - x_1)\, d\mathbf{r}_2 \tag{3.33}$$

Using the weak-coupling approximation $\rho_T^{(2)} = \rho^2 h$ and (3.17), one finds the correction to $\rho^{(1)}$ of order σ:

$$\delta\rho^{(1)}(x) = \sigma\kappa \exp(-\kappa x) \tag{3.34}$$

The surface charge density of the plasma is now $e\sigma$, as it should be:

$$\int_0^\infty \delta\rho^{(1)}(x)\, dx = \sigma \tag{3.35}$$

Note that (3.34) is just the well-known simple linearized Chapman–Gouy expression, which has to be added to the one-body density for an uncharged wall, as given by (3.27). A more sophisticated $\delta\rho^{(1)}$ cannot be obtained in the present weak-coupling theory.

4. THE WEAKLY COUPLED TWO-COMPONENT PLASMA

The theory of Section 3 can be easily generalized to a two-component symmetrical plasma, in two or three dimensions. We now consider a system of particles of charges e and $-e$, with equal number densities ρ. In the three-dimensional case at least, in addition to the Coulomb forces, there must be short-range repulsive forces between particles of opposite sign to prevent them from collapsing towards one another; however, within an approach *à la* Debye–Hückel, it is not necessary to consider explicitly these repulsive forces. The plane $x = 0$ is an uncharged hard wall.

One must now consider pair-correlation functions $h_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2)$, where the Greek indices denote the species ($+$ or $-$) of the particles. Equation (3.5) is replaced by the system

$$h_{\alpha\beta}(\mathbf{r}_1,\mathbf{r}_2) = -\beta\epsilon_{\alpha\beta}v(|\mathbf{r}_2-\mathbf{r}_1|) - \beta\rho\sum_{\gamma}\int_{x_3>0} h_{\alpha\gamma}(\mathbf{r}_1,\mathbf{r}_3)\epsilon_{\gamma\beta}v(|\mathbf{r}_2-\mathbf{r}_3|)\,d\mathbf{r}_3 \tag{4.1}$$

where v is still defined by (3.1); $\epsilon_{\alpha\beta}$ is $+1$ if $\alpha=\beta$ and -1 if $\alpha\neq\beta$. One sees at once from (4.1) that the symmetrical combinations vanish:

$$h_{++}+h_{+-}=h_{--}+h_{-+}=0 \tag{4.2}$$

The antisymmetrical combination

$$h_A = h_{++}-h_{+-}=h_{--}-h_{-+} \tag{4.3}$$

obeys the equation

$$h_A(\mathbf{r}_1,\mathbf{r}_2) = -2\beta v(|\mathbf{r}_2-\mathbf{r}_1|) - 2\beta\rho\int_{x_3>0} h_A(\mathbf{r}_1,\mathbf{r}_3)v(|\mathbf{r}_2-\mathbf{r}_3|)\,d\mathbf{r}_3 \tag{4.4}$$

The comparison between (3.5) and (4.4) shows that h_A has the same form as the function h considered in Section 3.1, provided the inverse Debye length κ is now defined as

$$\kappa = \left[4(\nu-1)\pi\beta e^2\rho\right]^{1/2} \tag{4.5}$$

instead of (3.8).

The linearized BGY equation (3.21) is replaced by the simpler equation

$$\nabla\rho_\alpha^{(1)}(x_1) = \beta e^2\rho^2\int_{x_2>0}\mathbf{F}(\mathbf{r}_1-\mathbf{r}_2)h_A(\mathbf{r}_1,\mathbf{r}_2)\,d\mathbf{r}_2 \tag{4.6}$$

(for symmetry reasons, near an uncharged wall, the one-body density $\rho_\alpha^{(1)}$ does not depend upon the species α, and the average electrical field $\mathbf{E}$ vanishes). With the definition (4.5) of κ, one now finds

$$f(x_1) = \beta e^2\rho^2\int_{x_2>0}F_x(\mathbf{r}_1-\mathbf{r}_2)h_A(\mathbf{r}_1,\mathbf{r}_2)\,d\mathbf{r}_2$$

$$= \frac{\kappa^4}{(\nu-1)4\pi}\int_0^\infty \frac{\exp\left[-2x_1(\kappa^2+l^2)^{1/2}\right]}{\left[(\kappa^2+l^2)^{1/2}+l\right]^2}\,l^{\nu-2}\,dl \tag{4.7}$$

and the solution of (4.6) is

$$\rho_\alpha^{(1)}(x)-\rho = -\int_x^\infty f(x)\,dx$$

$$= -\frac{\kappa^4}{(\nu-1)8\pi}\int_0^\infty \frac{\exp\left[-2x(\kappa^2+l^2)^{1/2}\right]}{(\kappa^2+l^2)^{1/2}\left[(\kappa^2+l^2)^{1/2}+l\right]^2}\,l^{\nu-2}\,dl \tag{4.8}$$

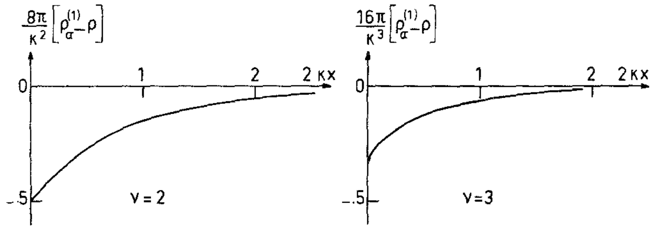

Fig. 2. The one-body densities for a weakly coupled symmetrical two-component plasma, in two ($\nu = 2$) or three ($\nu = 3$) dimensions, near an uncharged hard wall.

The integral (4.8) can be performed explicitly. One finds

$$\rho_\alpha^{(1)}(x) - \rho = -\frac{\kappa^2}{8\pi}\left[K_2(2\kappa x) - \left(\frac{1}{2\kappa^2 x^2} + \frac{1}{\kappa x}\right)\exp(-2\kappa x)\right] \qquad (\nu = 2)$$

$$\rho_\alpha^{(1)}(x) - \rho = -\frac{\kappa^3}{16\pi}\left[\left(\frac{1}{2\kappa^3 x^3} + \frac{1}{\kappa^2 x^2} + \frac{1}{2\kappa x}\right)\exp(-2\kappa x) - \frac{1}{\kappa x}K_2(2\kappa x)\right]$$

$$(\nu = 3) \qquad (4.9)$$

where K_2 is a Bessel function. These density profiles are shown in Fig. 2; they are monotonically increasing functions. The net charge density is everywhere zero:

$$e\left[\rho_+^{(1)}(x) - \rho_-^{(1)}(x)\right] = 0 \qquad (4.10)$$

When $x \to +\infty$, $\rho_\alpha^{(1)}(x) - \rho$ decays exponentially essentially as $\exp(-2\kappa x)$.

At the wall, the densities (4.9) become

$$\rho_\alpha^{(1)}(0) = \rho - \frac{\kappa^2}{16\pi} = \rho\left(1 - \frac{\beta e^2}{4}\right) \qquad (\nu = 2)$$

$$\rho_\alpha^{(1)}(0) = \rho - \frac{\kappa^3}{48\pi} \qquad (\nu = 3) \qquad (4.11)$$

Therefore, the pressures obtained from (4.11),

$$p = k_B T\left[\rho_+^{(1)}(0) + \rho_-^{(1)}(0)\right] \qquad (4.12)$$

do have the same values as the ones which are obtained by calculations in the bulk.[1,12]

If the hard wall carries a weak surface charge density $-e\sigma$, the same argument as in Section 3.3 shows that the correction to $\rho_\alpha^{(1)}$ of order σ is

$$\delta\rho_\pm^{(1)}(x) = \pm\sigma\frac{\kappa}{2}\exp(-\kappa x) \qquad (4.13)$$

The surface charge density of the plasma is $e\sigma$, as it should be:

$$\int_0^\infty e\left[\delta\rho_+^{(1)}(x) - \delta\rho_-^{(1)}(x)\right] dx = e\sigma \tag{4.14}$$

Again, (4.13) is just the simple linearized Chapman–Gouy expression.

5. CONCLUSION

We have studied the pair correlations near a plane wall. These correlations have a slow (algebraic) decay in the direction parallel to the wall.

Recently, sum rules for inhomogeneous Coulomb systems[14] have been proved under the assumption of a not too weak decay of the correlations; for instance, one of these sum rules states that the system formed by a particle plus its screening cloud has no electrical dipole moment. Although there are other very interesting nontrivial situations in which these sum rules hold, the underlying assumption about the decay rate of the correlations is *not* fulfilled in the cases which have been considered in the present paper, and some of the above-mentioned sum rules do not hold near a plane wall; for instance, the system formed by a particle plus its screening cloud does have a dipole moment.

For a two-dimensional system of particles interacting through a $1/r$ potential (electrons confined in a plane), the pair correlation function decays like r^{-3}, at least in the weak-coupling case.[15,16] It is rather natural to find the same decay rate near a wall, in the direction parallel to the wall, for a three-dimensional system with the same $1/r$ potential; since the screening cloud around a given particle is localized along the wall, it has indeed features reminiscent of a strictly two-dimensional geometry.

We have also studied the one-body density near a plane wall. The one-body density is related to the pair correlation function by the first BGY equation. For the two-dimensional one-component plasma at $\Gamma = 2$, we have exact expressions which of course satisfy the BGY equations. Less trivially, for weakly coupled plasmas, we have used the weak-coupling form of the pair correlation function in the first BGY equation in order to compute the weak-coupling form of the one-body density. Our approach is a consistent one, and it passes the test that the pressures $p^{(\theta)}$ in (3.32) or p in (4.12), obtained from the one-particle density near the wall, are each equal to the corresponding pressure obtained by a thermodynamical calculation in the bulk.

Many calculations of the one-body density near a plane wall have appeared in the literature.[17–22] Some of them[22] use a Poisson–Boltzmann equation for the pair correlation function, as we did in (3.6). However, it seems that the approximations in these approaches do not incorporate the specific feature of the weak decay of the correlations in the direction parallel to the wall. It might be that this feature is an essential one.

Some of our results in Sections 3 and 4 have been previously obtained by other authors.[23,24]

ACKNOWLEDGMENTS

The author is much indebted to J. L. Lebowitz for many stimulating discussions, and in particular for his suggestion to study the correlations near a wall.

APPENDIX: CHARGE DENSITY INDUCED BY A CHARGE SITTING OUTSIDE THE PLASMA

The calculations in Sections 2.2. and 3.1. can be easily extended for computing the charge density $C(\mathbf{r}_2|\mathbf{r}_1)$ at a point $\mathbf{r}_2$ inside the plasma $(x_2 > 0)$, when there is a particle at a point $\mathbf{r}_1$ outside the plasma $(x_1 < 0)$.

For the two-dimensional one-component plasma at $\Gamma = 2$,

$$C(\mathbf{r}_2|\mathbf{r}_1) = e\,\frac{\rho_T^{(2)}(\mathbf{r}_1, \mathbf{r}_2)}{\rho^{(1)}(\mathbf{r}_1)} \tag{A.1}$$

where $\rho^{(1)}$ and $\rho_T^{(2)}$ are given by (2.16) and (2.18), respectively. Now, $x_2 > 0$, $x_1 < 0$. An interesting limiting case is when $x_1 \to -\infty$, i.e., when the external particle is at a macroscopic distance from the plasma. One easily derives the corresponding behaviors

$$\rho^{(1)}(x_1) \sim \rho\,\frac{\exp(-2x_1^2)}{(2\pi)^{1/2}|x_1|} \tag{A.2}$$

$$\rho_T^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \sim -\rho^2 \exp\left[-(x_1 - x_2)^2\right]\left|\left(\frac{2}{\pi}\right)^{1/2} \frac{\exp\left[-(x_1 + x_2)^2/2\right]}{|x_1| + i(y_1 - y_2)}\right|^2 \tag{A.3}$$

Therefore,

$$C(\mathbf{r}_2|\mathbf{r}_1) \sim -2\left(\frac{2}{\pi}\right)^{1/2} e\rho\,\frac{|x_1|\exp(-2x_2^2)}{x_1^2 + (y_1 - y_2)^2} \tag{A.4}$$

The surface charge density then is

$$\int_0^\infty C(\mathbf{r}_2|\mathbf{r}_1)\,dx_2 \sim -\frac{e|x_1|}{\pi\left[x_1^2 + (y_1 - y_2)^2\right]} \tag{A.5}$$

and (A.5) is indeed what two-dimensional macroscopic electrostatics gives for the surface charge density induced in a semi-infinite conductor by a charge e located at a distance $|x_1|$ from that conductor.

For a weakly coupled one-component plasma,

$$C(\mathbf{r}_2|\mathbf{r}_1) = e\rho h(\mathbf{r}_1,\mathbf{r}_2) \tag{A.6}$$

h is given by (3.14), where, however, $\hat{h}(x_1,x_2,l)$ must now be computed in the case $x_1 < 0$. Some of the formulas of Section 3.1 have to be modified, and one now finds

$$\rho\hat{h}(x_1,x_2,l) = -\frac{\kappa^2}{(\kappa^2+l^2)^{1/2}+l}\exp\left[-l|x_1|-(\kappa^2+l^2)^{1/2}x_2\right] \qquad (x_1 \leqslant 0,\ x_2 \geqslant 0) \tag{A.7}$$

$$\rho\hat{h}(x_1,x_2,l) = \frac{\kappa^2}{2l}\left\{\frac{(\kappa^2+l^2)^{1/2}-l}{(\kappa^2+l^2)^{1/2}+l}\exp\left[-l(|x_1|+|x_2|)\right] - \exp(-l|x_1-x_2|)\right\} \qquad (x_1,x_2 \leqslant 0) \tag{A.8}$$

The induced charge density (A.6) is given by using (A.7) in (3.14). If (A.8) is used in (3.14), $-(\beta e)^{-1}h(\mathbf{r}_1,\mathbf{r}_2)$ is the electrostatic potential at $\mathbf{r}_2$ outside the plasma. More explicit formulas are easily found in the limiting case $x_1 \to -\infty$, i.e., when the distance $|x_1|$ is macroscopic. The corresponding behaviors are

$$e\rho h(\mathbf{r}_1,\mathbf{r}_2) \sim -\frac{\kappa|x_1|\exp(-\kappa x_2)}{(\nu-1)\pi\left[x_1^2+(\mathbf{y}_1-\mathbf{y}_2)^2\right]^{\nu/2}} \qquad (x_1 \leqslant 0,\ x_2 \geqslant 0) \tag{A.9}$$

$$-\frac{1}{\beta e}h(\mathbf{r}_1,\mathbf{r}_2) \sim \frac{1}{e}\left\{v(|\mathbf{r}_1-\mathbf{r}_2|) - v\left(\left[(x_1+x_2)^2+(\mathbf{y}_1-\mathbf{y}_2)^2\right]^{1/2}\right)\right\} \qquad (x_1,x_2 \leqslant 0) \tag{A.10}$$

where v is the potential (3.1). The surface charge density then is

$$\int_0^{\infty} e\rho h(\mathbf{r}_1,\mathbf{r}_2)\,dx_2 = -\frac{e|x_1|}{(\nu-1)\pi\left[x_1^2+(\mathbf{y}_1-\mathbf{y}_2)^2\right]^{\nu/2}} \tag{A.11}$$

Again, (A.10) and (A.11) are indeed the correct expressions from macroscopic electrostatics; (A.10) is the electrostatic potential outside a semi-infinite conductor when a charge e is located at a distance $|x_1|$ from this conductor (i.e., the potential of the charge plus the potential of its image), and (A.11) is the surface charge density on the conductor.

It may be noted that, when $|\mathbf{y}_2 - \mathbf{y}_1| \to \infty$, the induced charge density (A.4) or (A.9) behaves like $|\mathbf{y}_2 - \mathbf{y}_1|^{-\nu}$ also in the present case.

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