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# Mean spherical approximation for charged hard spheres near a charged hard wall in a neutralizing background

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The distribution of charged hard spheres near a charged surface in a nonuniform neutralizing background is calculated using the integral equation method based on the mean spherical approximation for both bulk and surface direct correlation functions. The contact value of the distribution and the total electric potential drop are given and compared to the exact result. Various possible extensions of the model are discussed.

## I. INTRODUCTION

In the last few years, there has been extensive work concerning the distribution of charged particles near a charged hard wall (see for instance Refs. 1-3). Binary ionic mixtures are usually considered, since the main purpose of these studies is to obtain a better microscopic description of the electrolyte-electrode system. On the other hand, there has been little interest for the charged one-component system in a neutralizing background, although this model may give some qualitative features of the ionic profile of liquid metals near a surface.

In this paper, we consider the case of charged hard spheres embedded in a fixed nonuniform background. For the bulk fluid, Palmer and Weeks,<sup>4</sup> using the mean spherical approximation, have given analytic expressions for the direct correlation function, the Laplace transform of the radial distribution function, and some thermodynamic properties. Hansen and Weis<sup>5</sup> have made comparison of these results with Monte Carlo computation.

We give here the solution of the Ornstein-Zernike equation for this fluid in contact with a charged hard wall, following the procedure introduced by Henderson *et al.*<sup>6</sup> and Blum and Stell.<sup>7</sup> The wall-ion and the bulk ion-ion direct correlation functions are both described by MSA closures.

In Sec. II, basic relations are established and the method of solution is given in Sec. III. Analytic expressions are obtained for the ionic profile, its contact value and the total electric potential drop. When an external charge is present a differential capacity is defined and calculated. In the last section, we discuss some numerical results and consider the possible extensions of the model.

## II. BASIC RELATIONS

We consider a classical system of ions of number density  $\rho$ , embedded in a neutralizing background characterized by a density distribution  $n(z)$ , where  $0z$  is the direction normal to the surface.

The interaction potential between ions is given by

$$\begin{aligned} v(r) &= \infty, & r < \sigma, \\ &= Z^2 e^2 / r, & r > \sigma, \end{aligned} \quad (1.1)$$

where  $Ze$  is the ionic charge and  $\sigma$  the ionic diameter. It is convenient to introduce the usual variables

$$\eta = (\pi/6) \rho \sigma^3 \quad \text{and} \quad \kappa = (4\pi Z^2 e^2 \rho \beta)^{1/2}.$$

$\kappa$  is the Debye Hückel inverse screening length.

In the bulk ( $z \rightarrow +\infty$ )  $n(z) \rightarrow n$  and  $n = \rho Z$  to preserve electroneutrality. An impenetrable planar wall for the ions is placed at  $z = -\sigma/2$ , so the ionic profile  $\rho(z)$  vanishes for  $z < 0$ .

For simplicity, we take the dielectric constant equal to unity in the whole space. Doing that we neglect effects such as dielectric saturation or image interaction with the wall which would require a much more sophisticated treatment.

On the other hand, one can have  $n(z) \neq 0$  for  $z < 0$  to give the possibility for the background to penetrate the wall. This kind of model was recently proposed<sup>8</sup> to represent the ideally polarizable electrode. In this case the background simulates a highly degenerate electron gas.

For the wall-particle correlation function  $h(z) = \rho(z)/\rho - 1$ , we can write an Ornstein-Zernike equation<sup>6</sup>

$$h(z) = C(z) + \rho \int d\mathbf{r}' C_B(|\mathbf{r} - \mathbf{r}'|) h(z'), \quad (1.2)$$

where  $C_B(r)$  is the interionic bulk direct correlation function and  $C(z)$  the wall-ion direct correlation function.

With our model, the nonuniform background is equivalent to an external potential  $\phi(z)$ , so we can do the decomposition

$$C(z) = C^0(z) - \beta Ze \phi(z), \quad (1.3)$$

where  $C^0(z)$  is supposed to be a short-range function. We then adopt a MSA closure for the wall-ion direct correlation function

$$C^0(z) = 0, \quad z > 0. \quad (1.4)$$

The potential  $\phi(z)$  can be unambiguously determined by considering Eq. (1.2) as a special case of the two-components Ornstein-Zernike equation

$$\begin{aligned} h(z) &= C^0(z) + \rho \int d\mathbf{r}' C_B(|\mathbf{r} - \mathbf{r}'|) h(z') \\ &\quad + n \int d\mathbf{r}' C_{B,e}(|\mathbf{r} - \mathbf{r}'|) h_e(z'), \end{aligned} \quad (1.5)$$

where  $nh_s(z) = n(z) - n$  and  $C_{B,s}(r)$ , the background-ion bulk direct correlation function, is chosen as purely Coulombic

$$C_{B,s}(r) = \beta Ze^2/r. \quad (1.6)$$

Another choice that we do not consider here would be the introduction of a pseudopotential in Eq. (1.6). From Eqs. (1.2), (1.3), and (1.5) we see that

$$\phi(z) = -e \int d\mathbf{r}' \frac{nh_s(z)}{|\mathbf{r} - \mathbf{r}'|}. \quad (1.7)$$

For the planar interface this expression is diverging but a cancellation occurs with a similar divergence in the second term of Eq. (1.2).

Introducing the usual decomposition

$$C_B(r) = C_B^0(r) - \beta Z^2 e^2/r \quad (1.8)$$

and the total mean electrostatic potential

$$\psi(z) = -4\pi e \int_z^\infty dt(t-z)[Z\rho(t) - n(t)]. \quad (1.9)$$

Equation (1.2) becomes after some manipulations

$$h(z) = -\beta Ze\psi(z) + C^0(z) + 2\pi\rho \int_0^\infty dt t C_B^0(t) \int_{z-t}^{z+t} du h(u). \quad (1.10)$$

If we take  $C_B^0(r) = 0$  in Eq. (1.10) we recover the linearized Poisson-Boltzmann equations

$$\begin{aligned} h(z) &= -\beta Ze\psi(z), \quad z > 0, \\ \nabla^2 \psi(z) &= -4\pi e[Z\rho(z) - n(z)]. \end{aligned} \quad (1.11)$$

A better approximation is the MSA

$$C_B^0(r) = 0, \quad r > \sigma, \quad (1.12)$$

which also has the advantage of giving analytical results for the bulk fluid.<sup>4</sup>

With the closure relations (1.4) and (1.12), Eq. (1.10) represents a MSA/MSA treatment of the profile  $\rho(z)$ . We give now the solution of this equation.

### III. SOLUTION

The procedure for finding the solution of Eq. (1.10) follows the great lines of the analysis recently reviewed in Ref. 9. Nevertheless, we quote here the main steps of the analytical development, since the systems in consideration are not identical. Consider the Fourier transform of Eq. (1.10)

$$h(k) = C^0(k) - \beta Ze\psi(k) + \rho C_B^0(k)h(k), \quad (2.1)$$

where

$$h(k) = \int_{-\infty}^{\infty} dz \exp(ikz) h(z),$$

$$C^0(k) = \int_{-\infty}^0 dz \exp(ikz) C^0(z), \quad \text{since } C^0(z) = 0 \text{ for } z > 0,$$

$$\psi(k) = \int_{-\infty}^{\infty} dz \exp(ikz) \psi(z),$$

and

$$C_B^0(k) = \frac{4\pi}{k} \int_0^\infty dr \sin kr r C_B^0(r).$$

In all these integrals  $\text{Im } k = -\delta$  ( $\delta > 0$ ) to ensure convergence for  $z \rightarrow -\infty$ . Using the definitions of  $\psi$ ,  $\phi$ , and  $C^0(k)$ , Eq. (2.1) can be put in the equivalent form

$$h(k)[1 - \rho C_B(k)] = C^0(k) - \beta Ze\phi(k). \quad (2.2)$$

In calculating the solution of Eq. (2.2) divergence problems occur from the use of Coulombic potential, which can be avoided by the use of a Yukawa potential  $\exp(-\mu r)/r$ . The limit  $\mu \rightarrow 0$  will be taken at the end of the calculation following the procedure indicated in Ref. 10.

From Eq. (1.7) we get

$$\phi(k) = -\frac{4\pi en}{k^2 + \mu^2} h_s(k), \quad (2.3)$$

where

$$nh_s(k) = \int_{-\infty}^{\infty} [n(z) - n] \exp(ikz) dz.$$

Eq. (2.2) can be solved by a procedure developed by Blum and Stell,<sup>7</sup> using the Baxter factorization technique.<sup>11</sup> It can be shown that the bulk direct correlation function can be factorized in the form

$$1 - \rho C_B(k) = Q(k)Q(-k), \quad (2.4)$$

with

$$Q(k) = 1 - \rho \int_0^\infty dr Q(r) \exp(ikr),$$

where  $Q(k)$  is the Baxter function.

For a two-component charged system, the Baxter's functions have been calculated in order to solve the MSA.<sup>10</sup> This work has not been done for the one-component system in a uniform background and we give in Appendix A the main results and properties of  $Q(r)$ .

We get

$$\begin{aligned} Q(r) &= Q_0(r), \quad r \leq \sigma, \\ &= -A \exp(-\mu r), \quad r > \sigma. \end{aligned} \quad (2.5)$$

For the purely Coulombic case ( $\mu \rightarrow 0$ )  $Q_0(r)$  is a cubic polynomial in  $r$ , whereas it is only quadratic in the two-components case. This complication is not surprising since, as noted by Palmer and Weeks,<sup>4</sup> the one-component system is a simple example of an assembly of particles with nonadditive diameters.

Using Eqs. (2.3) and (2.4), we may now rewrite Eq. (2.2)

$$h(k)Q(k) = \left[ C^0(k) + \frac{\kappa^2}{k^2 + \mu^2} h_s(k) \right] Q(-k)^{-1}. \quad (2.6)$$

Consider now the Fourier inverse of this equation for  $z > 0$

$$\begin{aligned} h(z) - \rho \int_0^\infty dr h(z-r)Q(r) &= \frac{1}{2\pi} \int_{-\infty-i\delta}^{\infty-i\delta} C^0(k) Q(-k)^{-1} \exp(-ikz) dk \\ &+ \frac{\kappa^2}{2\pi} \int_{-\infty-i\delta}^{\infty-i\delta} \frac{h_s(k) Q(-k)^{-1}}{k^2 + \mu^2} \exp(-ikz) dk. \end{aligned} \quad (2.7)$$

As in Ref. 7, we seek solutions such that the function  $C^0(k)$  is bounded and has no singularities in the complex half-plane  $\text{Im } k = \delta$ . Then it can be shown that the first integral in the right-hand side of Eq. (2.7) gives no contribution for  $z > 0$ . We thus have

$$h(z) - \rho \int_0^\infty dr h(z-r) Q(r) = \frac{\kappa^2}{2\pi} \int_{-\infty-i\delta}^{+\infty-i\delta} \frac{h_0(k) Q(-k)^{-1}}{k^2 + \mu^2} \times \exp(-ikz) dk, \quad (2.8)$$

for  $z > 0$ .

Using Eq. (2.5), the Laplace transform of Eq. (2.8) is straightforward and yields

$$[1 - \rho Q(s)] h(s) - \frac{\rho}{s} Q(s) + \frac{\rho}{s} \int_0^\sigma Q_0(r) dr - \frac{\rho A}{\mu s} \exp(-\mu\sigma) = \frac{\kappa^2}{2\pi} \int_{-\infty-i\delta}^{+\infty-i\delta} \frac{h_0(k) Q(-k)^{-1}}{(k^2 + \mu^2)(s + ik)}, \quad (2.9)$$

where

$$h(s) = \int_0^\infty \exp(-sz) h(z) dz,$$

$$Q(s) = \int_0^\infty \exp(-sr) Q(r) dr.$$

$$I(s) = \kappa^2 \text{Re } s \left[ \frac{\exp(ika)}{ik(k^2 + \mu^2)(s + ik)} \times \frac{1}{\left[ 1 - \rho \int_0^\sigma dr \exp(-ikr) Q_0(r) + \rho A \frac{\exp(-(ik + \mu)\sigma)}{ik + \mu} \right]} \right]_{k \rightarrow -i\mu}. \quad (2.12)$$

In the limit  $\mu \rightarrow 0$ , a careful analysis of this term leads to the result

$$I(s) = -\frac{\kappa}{\mu s} - \frac{\kappa}{s} \left[ a + \sigma - \frac{1}{\kappa} - \frac{1}{s} + \frac{\rho}{\kappa} \int_0^\sigma dr Q_0(r) \right] + O(\mu), \quad (2.13)$$

where Eq. (A1) and (A2) have been used.

Letting  $\mu \rightarrow 0$ , we get from Eq. (2.9) with the help of Eq. (A2)

$$[1 - \rho Q(s)] h(s) = \frac{\rho}{s} Q(s) + \frac{\kappa}{s^2} - \frac{\rho}{s} \int_0^\sigma Q_0(r) dr - \frac{\kappa}{s} (a + \sigma). \quad (2.14)$$

Finally, we find for the Laplace transform of the normalized profile  $g(z) = h(z) + 1$

$$g(s) = \frac{1 + (\kappa/s) - \rho \int_0^\sigma Q_0(r) dr - \kappa(a + \sigma)}{s[1 - \rho Q(s)]}. \quad (2.15)$$

This formula gives the solution of our stated model, together with Eqs. (A4), (A5), and (A6).

Taking the limit  $s \rightarrow 0$  [see Eq. (A7)] one finds immediately

$$\lim_{s \rightarrow 0} h(s) = -a, \quad (2.16)$$

which is nothing but the electroneutrality condition.

In Sec. IV, we shall do the inversion into the real space and give a zone-by-zone representation of the

The calculation of the integral in the right-hand side of Eq. (2.9) needs the specification of the background profile  $n(z)$ . To simplify at first time, we take

$$n(z) = n\theta(z - a), \quad (2.10)$$

where  $\theta(z)$  is the unit step function. A nonuniform profile will be considered further.

The integral in Eq. (2.9) thus becomes

$$I(s) = -\frac{\kappa^2}{2\pi} \int_{-\infty-i\delta}^{+\infty-i\delta} dk \frac{\exp(ika)}{ik(k^2 + \mu^2)} \frac{Q(-k)^{-1}}{(s + ik)}. \quad (2.11)$$

$Q(-k)$  is known<sup>7</sup> to have no zeros in the lower half complex  $k$  plane. Therefore, if  $a < 0$ , we can close a contour around the lower  $k$  plane and Eq. (2.11) can be calculated using Cauchy's residue theorem with the only pole  $k = -i\mu$ .

On the other hand, a positive value of  $a$  would require a study of the integrand in the upper  $k$  plane, where the determination of the zeros of  $Q(-k)$  is a difficult task. For simplicity we shall not consider this case in this paper. Using Eqs. (2.4) and (2.5) we have

wall-particle profile. However, we can readily obtain the contact value  $g(0)$  and the potential drop across the interface  $\Delta\psi = \psi(\infty) - \psi(-\infty)$ .

From Eq. (2.8) and recalling that  $h(z) = -1$ , if  $z < 0$  we get

$$g(0) = 1 - \rho \int_0^\infty dr Q(r) dr - \frac{\kappa^2}{2\pi} \int_{-\infty-i\delta}^{+\infty-i\delta} dk \times \frac{\exp(ika) Q(-k)^{-1}}{ik(k^2 + \mu^2)}. \quad (2.17)$$

In the limit  $\mu \rightarrow 0$ , we find

$$g(0) = 1 - \kappa(a + \sigma) - \rho \int_0^\sigma dr Q_0(r) \quad (2.18)$$

and from Eq. (A4) we obtain

$$g(0) = \frac{1 + 2\eta}{2(1 - \eta)^2} \left\{ 1 + \left[ 1 + \frac{2\kappa\sigma(1 - \eta)^2}{(1 + 2\eta)^2} \right]^{1/2} \right\} - \kappa \left( a + \frac{\sigma}{2} \right). \quad (2.19)$$

The potential drop is

$$\Delta\psi = -4\pi e \int_{-\infty}^0 n(z) z dz + 4\pi e \int_0^\infty z [Z\rho g(z) - n(z)] dz = 4\pi e Z\rho \left\{ \frac{a^2}{2} - \lim_{s \rightarrow 0} \frac{d}{ds} [h(s)] \right\}. \quad (2.20)$$

Using Eq. (A7) we get after some manipulations

$$\beta Ze\Delta\psi = \frac{\kappa^2 a^2}{2} + \kappa\sigma \left\{ \frac{2\eta^2 + 2 - 13\eta}{12(1-\eta)^2} - \frac{\kappa\sigma(\eta-10)}{60} - \frac{2+\eta}{12(1-\eta)^2} \mathcal{R} \right. \\ \left. - \frac{a}{\sigma} \left[ -\frac{\kappa\sigma}{2} + \frac{1+2\eta}{2(1-\eta)^2} \left( 1 + \frac{\mathcal{R}}{1+2\eta} \right) \right] \right\}, \quad (2.21)$$

where  $\mathcal{R}$  is defined by Eq. (A3).

As noted before, it is only for simplicity that we took a step profile for the neutralizing background. Nevertheless, a more refined choice can be done. For instance a very usual form is <sup>8,12</sup>

$$n(z) = n \exp(\alpha(z-a)), \quad z < a, \\ = n \left[ 1 - \frac{\exp(-\alpha(z-a))}{2} \right], \quad z > a. \quad (2.22)$$

Eq. (2.11) thus becomes

$$I(s) = -\frac{\kappa^2}{2\pi} \int_{-\infty-i0}^{+\infty-i0} dk \frac{\exp(ika)}{ik(k^2 + \mu^2)(\alpha^2 + k^2)} \frac{Q(-k)^{-1}}{(s+ik)}, \quad (2.23)$$

where we see the appearance of the pole  $k = -i\alpha$  coming from  $n(z)$ .

We give in Appendix B the new formulas for  $g(s)$ ,  $g(o)$ , and  $\Delta\psi$ .

All these results can be easily extended to the case when exists an extra-charge distribution  $q(z) = q\delta(z-b)$  ( $b < 0$ ), where  $q$  is the surface charge density and  $\delta(z)$  the Dirac function.

In Eq. (2.3) we have now to consider an extra term

$$\phi_1(k) = \frac{4\pi q}{k^2 + \mu^2} \exp(ikb), \quad (2.24)$$

which gives an extra contribution for  $I(s)$  in Eq. (2.11)

$$I_1(s) = -2\beta Zeq \int_{-\infty-i0}^{+\infty-i0} dk \frac{\exp(ikb)Q(-k)^{-1}}{(k^2 + \mu^2)(s+ik)}. \quad (2.25)$$

It is then easy to see that in the limit  $\mu \rightarrow 0$  the result does not depend on  $b$ , and we obtain for  $g(s)$  the same result as Eq. (2.15) with  $a$  replaced by  $a + q/ne$ . This result is not surprising since  $q + nea$  is the total charge density per unit area in the left side of the wall, and we expect the profile for  $z > 0$  not to depend on the details of the charge distribution on the other side of the wall. The same correction has to be done for  $g(o)$  and for  $\Delta\psi$  in the last term. Moreover, in this last expression, one must add  $4\pi qb \times \beta Ze$ , where  $4\pi qb$  represents the potential drop due to the charged plane located at  $z = b$ .

To define a differential capacitance for the system, one needs a physical model for the charged background to explicit the eventual dependance of  $a$  with the external charge  $q$ . If one supposes that  $a$  and  $b$  are independent of  $q$ , the capacity  $C$  is readily obtained

$$\frac{1}{4\pi C} = \frac{1}{4\pi} \left( \frac{\partial \Delta\psi}{\partial q} \right)_\sigma = b + \frac{1}{2\kappa} - \frac{1}{\kappa^2 \sigma} \frac{1+2\eta}{2(1-\eta)^2} \left( 1 + \frac{\mathcal{R}}{1+2\eta} \right). \quad (2.26)$$

#### IV. RESULTS AND DISCUSSION

Let us first consider the Laplace inversion of Eq. (2.15)

$$g(z) = \frac{1}{2\pi i} \int_C g(s) \exp(sz) ds \\ = \frac{1}{2\pi i} \int_C \frac{1 + \frac{\kappa}{s} - \rho \int_0^\sigma Q_0(r) dr - \kappa(a+\sigma)}{s[1-\rho Q(s)]} \exp(sz) ds, \quad (3.1)$$

where  $C$  is the Bromwich's contour.

As indicated in Appendix A, we can write

$$1 - \rho Q(s) = \frac{S(s\sigma) + \exp(-s\sigma)L(s\sigma)}{(1-\eta)^2(s\sigma)^4}, \quad (3.2)$$

where  $S(s\sigma)$  and  $L(s\sigma)$  are respectively fourth-order and second-order polynomials in  $s\sigma$ . This decomposition is identical to the result given in Ref. 4.

The Laplace inversion [Eq. (3.1)] yields the usual "zone-by-zone" representation of  $g(z)$ . It comes from the observation that for  $\text{Re}(s) > 0$

$$|L(s\sigma) \exp(-s\sigma)/S(s\sigma)| < 1. \quad (3.3)$$

Thus we have

$$\frac{1}{1 - \rho Q(s)} = \frac{(1-\eta)^2(s\sigma)^4}{S(s\sigma)} \sum_{n=0}^{\infty} \left[ -\frac{L(s\sigma)}{S(s\sigma)} \exp(-s\sigma) \right]^n \quad (3.4)$$

and for the Laplace inverse of Eq. (3.1) we only need the four roots of  $S(s\sigma)$  and the corresponding residues.

The algebraic calculation becomes much simpler and illuminating when  $\kappa\sigma$  is a small quantity. More precisely if

$$\frac{2\kappa\sigma(1-\eta)^3}{(1+2\eta)^2} \ll 1, \quad (3.5)$$

one can expand the radical  $\mathcal{R}$

$$\mathcal{R} \sim (1+2\eta) + \kappa\sigma \frac{(1-\eta)^3}{1+2\eta}. \quad (3.6)$$

Then the correlation factor  $Q(s)$  decouples exactly into the hard core and electrostatic parts

$$1 - \rho Q(s) = \frac{1}{(1-\eta)^2(s\sigma)^4} \left[ s\sigma + \frac{(1-\eta)^2}{1+2\eta} \kappa\sigma \right] [S_0(s\sigma) + \exp(-s\sigma)L_0(s\sigma)], \quad (3.7)$$

where  $S_0$  and  $L_0$  are the corresponding polynomials of the hard-spheres system. The roots of  $S_0$  were calculated by Wertheim.<sup>13</sup>

It is clear from Eqs. (3.1) and (3.7) that the length  $\lambda = [(1+2\eta)/(1-\eta)^2]1/\kappa$ , which comes only from Coulomb potential gives an exponential behavior in  $g(z)$ . On the other hand, the hard-core part has an oscillatory character which modulates the shape of the profile.

Figure 1 illustrates this behavior for  $\eta = 0.45$ ,  $\kappa\sigma = 1$ , and  $a = -\sigma/2$ , up to the distance  $z = 2\sigma$  from the wall. In fact, in this zone the profile is quite similar to the hard-spheres one.

When  $\kappa\sigma$  increases, Eq. (3.5) is no more verified and the pleasant separation between electrostatic and hard core contributions occurs no more. From Fig. 1 we see that for  $\kappa\sigma = 10$ , the most important effects take place in the zone  $0 - \sigma$ . For greater  $\kappa\sigma$  and  $\eta$  still 0.45 the

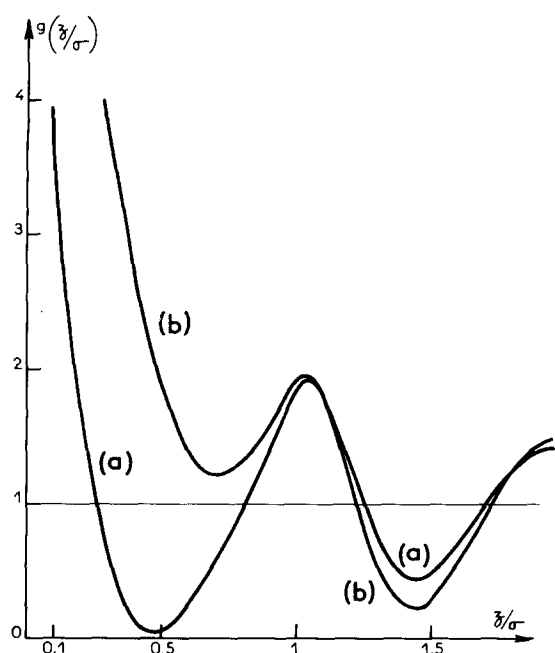


FIG. 1. Normalized ionic profile  $g(z) = [\rho(z)/\rho]$  as a function of the reduced distance  $z/\sigma$  to the hard wall. (a)  $\kappa\sigma = 1$ ,  $g(o) = 6.42$  and (b)  $\kappa\sigma = 10$ ,  $g(o) = 7.49$ . For both curves  $\eta = 0.45$  and  $a = -\sigma/2$ .

model may become qualitatively bad and induce negative parts in  $g(z)$ : this failure comes from the MSA closure (see below).

We have also considered the case of small ions. In Fig. 2 the ionic profile for  $\eta = 0.1$  and  $\kappa\sigma = 13.45$  [this corresponds to  $\Gamma = (\kappa\sigma)^2/12\eta^{2/3} = 70$ ] is compared to the

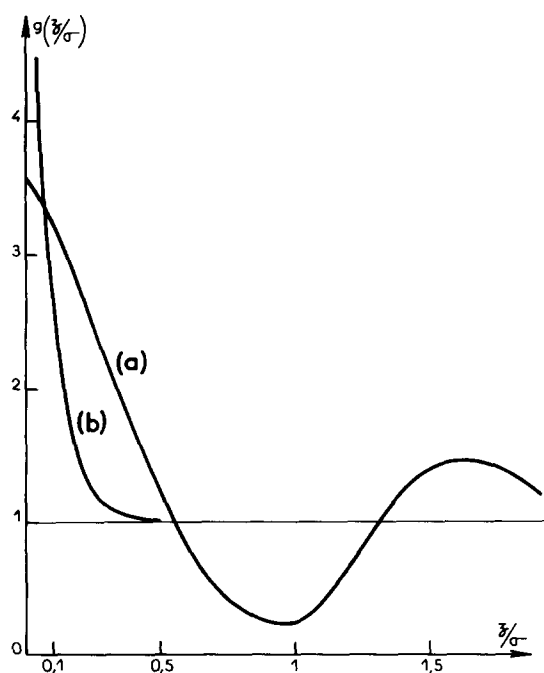


FIG. 2. Normalized ionic profile as a function of  $z/\sigma$ . (a) MSA results  $g(o) = 3.58$ , (b) Poisson-Boltzmann results [Eq. (1.11)],  $g(o) = 7.73$ . The values of the parameters are  $\eta = 0.1$  and  $\kappa\sigma = 13.45$ .

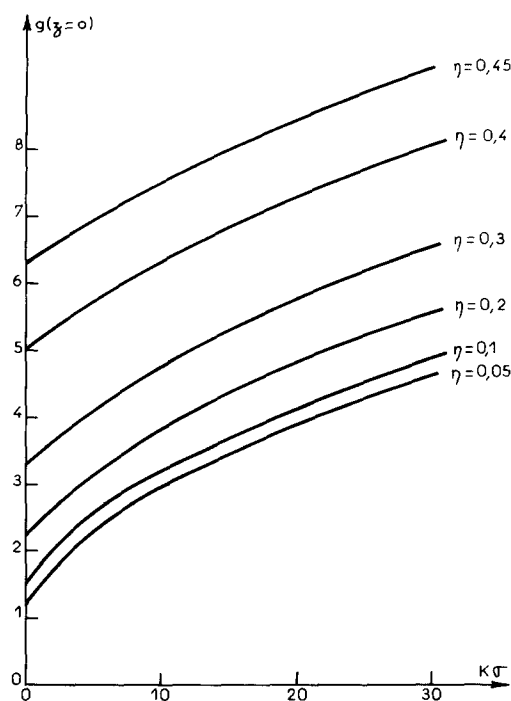


FIG. 3. Variations of the contact value  $g(z=0)$ , with respect to  $\kappa\sigma$  for different choices of the packing fraction  $\eta$ . The hard wall is located in  $a = -\sigma/2$ .

Poisson-Boltzmann profile solution of Eq. (1.11). We see that even for this small value of  $\eta$ , the profile is strongly structured and totally different of the P.B. profile. This can be related to the bulk case<sup>5,14</sup> where the radial distribution function is shifted away from the origin when  $\kappa\sigma$  increases. This reveals an overall increase in structure due to Coulombic interactions. With these values of  $\eta$  and  $\kappa\sigma$ , this kind of model may describe a liquid metal in a first order perturbation theory.

Let us now discuss the contact value  $g(o)$  and the potential drop  $\Delta\psi$ . If  $\kappa = 0$ , one recovers from Eq. (2.19) the Percus-Yevick result for hard spheres near a hard wall<sup>6</sup>

$$g(0) = \frac{1 + 2\eta}{(1 - \eta)^2} \quad (3.8)$$

Figure 3 shows the variations of  $g(o)$  with respect to  $\kappa\sigma$  for different values of  $\eta$  and for  $a = -\sigma/2$ . It is clear from Eq. (2.19) that the curves need only to be shifted when  $a$  varies. In Fig. 4 we plot the reduced potential drop  $\beta Ze\Delta\psi$  versus  $\kappa\sigma$  for  $a = -\sigma/2$ , and we can notice that  $\Delta\psi$  does not exhibit a strong dependence with the packing fraction  $\eta$ .

The problem of the validity of these results have to be considered, since we use MSA closures for both bulk and surface direct correlation functions.

In the bulk fluid, the MSA gives rather poor results for the contact value of the radial distribution function  $g_B(r)$ , but comparison with Monte Carlo computations<sup>5</sup> shows satisfactory agreement as long as  $r$  is not too small and  $\kappa\sigma$  not too high. Although the HNC approximation gives better results, we believe that the MSA

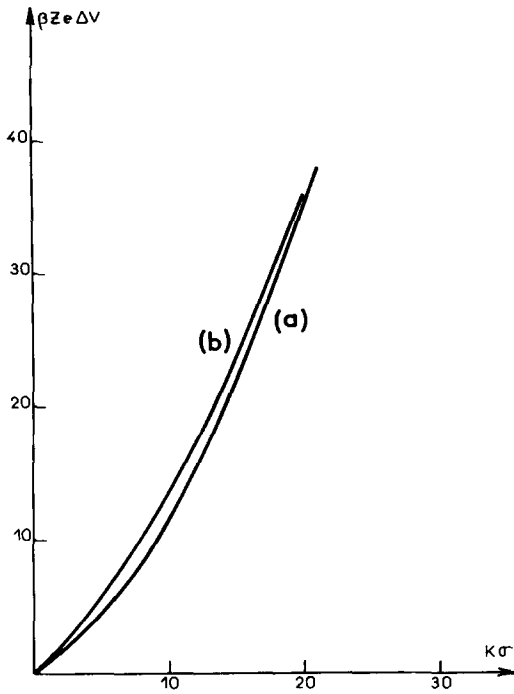


FIG. 4. Variations of the reduced electric potential drop  $\beta Z e \Delta \psi$  as a function of  $\kappa \sigma$ ;  $a = -\sigma/2$ . (a)  $\eta = 0.05$  and (b)  $\eta = 0.45$ .

$g_B(r)$  and  $c_B(r)$  are reliable enough to be used in the surface problem, the more so as it has the advantage to permit analytical calculations. The MSA closure for the wall-particle direct correlation function is more questionable.

The failure of this approximation is quite visible in Eq. (2.19), since negative values of  $g(o)$  can occur when  $a > -\sigma/2$ . In the same way the potential drop  $\Delta \psi$  is likely to be wrong for some values of  $\eta$ ,  $\kappa \sigma$ , or  $a$ .

Recently an exact relation between  $g(o)$  and  $\Delta \psi$  have been given in the literature.<sup>15</sup> It is a direct extension of Henderson *et al.*<sup>16</sup> result to a one-component system in a charged compensating background.

With our notations it simply reads

$$g(o) - \beta Z e \Delta \psi = \frac{P}{\rho k T}, \quad (3.9)$$

when there exists no external electric field.

$P$  is the bulk pressure, given in the MSA by

$$\begin{aligned} \frac{P}{\rho k T} = & 1 + \frac{4\eta(1+\eta/2)}{(1-\eta)^2} - \frac{1}{6} \frac{(1+2\eta)^2}{(1-\eta)^2} \left[ 1 - \frac{R}{(1+2\eta)} \right]^2 \\ & - \frac{1}{72\eta} \left[ \left( 1 + \eta - \frac{\eta^2}{5} \right) (\kappa \sigma)^2 + (1+2\eta) \kappa \sigma - 6\kappa \sigma \right]. \end{aligned} \quad (3.10)$$

It is clear that Eqs. (2.19) and (2.21) do not verify Eq. (3.9), at least because of their dependence with  $a$ , since  $P/\rho k T$  is independent of this last quantity.

Qualitatively, for  $\eta = 0.45$  and  $\kappa \sigma = 1$ , the left-hand side of Eq. (3.9) gives 5.4 when  $P/\rho k T = 8.2$ ; for  $\kappa \sigma = 10$  it gives -6.0 when  $P/\rho k T = 3.9$ ; for  $\eta = 0.1$  and

$\kappa \sigma = 13.45$  it gives -15.9 when  $P/\rho k T = -22.1$ .

These results cannot be considered as satisfactory. The reason of this disagreement can be guessed from the approximation inherent to the closure (1.4).

We know from the work of Wertheim<sup>17</sup> that in a non-uniform fluid  $\rho(r)$  satisfies the exact equation

$$k T \nabla \ln \rho(r) = -\nabla V_{\text{ext}}(r) + k T \int d\mathbf{r}' C(\mathbf{r}, \mathbf{r}') \nabla \rho(r'), \quad (3.11)$$

where  $C(\mathbf{r}, \mathbf{r}')$  is the nonuniform direct correlation function. In our case, we get

$$\frac{d}{dz} \ln[1+h(z)] = -\beta Z e \frac{d\psi}{dz} + \rho \int d\mathbf{r}' C^0(\mathbf{r}, \mathbf{r}') \frac{d}{dz'} h(z'), \quad (3.12)$$

where  $C^0(\mathbf{r}, \mathbf{r}')$  is the non-Coulombic part of  $C(\mathbf{r}, \mathbf{r}')$ :

$$C^0(\mathbf{r}, \mathbf{r}') = C(\mathbf{r}, \mathbf{r}') + \frac{\beta Z^2 e^2}{|\mathbf{r} - \mathbf{r}'|}. \quad (3.13)$$

The comparison with Eqs. (1.2) and (1.10) clearly shows that in using the MSA closure [Eq. (1.4)], we make the approximation  $C^0(\mathbf{r}, \mathbf{r}') = C_B^0(|\mathbf{r} - \mathbf{r}'|)$  and we expand the logarithm  $\ln[1+h(z)] \sim h(z)$ . If this last approximation is not made, one would have a HNC closure for the wall-particle direct correlation function. The corresponding values of  $g(o)$  and  $\Delta \psi$  would probably be better but the analytical calculation is no more available.

Some kind of "exponential" approximation is suggested for  $g(z)$  in the case of binary mixtures.<sup>1</sup> For our one-component system this approximation seems difficult to justify since no natural separation occurs between the hard-sphere and the Coulombic contributions.

Remaining in the frame of Eq. (1.10) another way to improve the results is the technique of the GMSA (see, for instance Refs. 9, 18, and 19). We can assume  $C^0(z) = M \exp(-mz)$  for  $z > 0$  instead of  $C^0(z) = 0$ . One of the unknown coefficients  $M$  or  $m$  can then be adjusted in order to satisfy the exact relation (3.9). However, contrary to the pure hard-sphere case, no other exact relation is available.<sup>19</sup> On the other hand, this technique has the great advantage to give analytical results like the MSA.

Finally, we wish to emphasize that, in spite of the crudeness of the approximations, this model may be a first step to describe some qualitative features of the ionic profile of liquid metals near a charged wall.

We can also remark that the above equations can describe the behavior of the classical one-component plasma (OCP) near a wall, since the MSA bulk correlation functions of the charged hard spheres system are a good approximation of the exact OCP correlation functions for high  $\Gamma$ .<sup>20</sup>

## APPENDIX A

In this appendix, we give the main results concerning the Baxter correlation factor  $Q(r)$ , defined by Eq. (2.4).

The calculation follows the lines of Blum's method.<sup>10</sup> We get

$$Q(r) = Q_0(r), \quad r \leq \sigma, \\ = -A \exp(-\mu r), \quad r > \sigma, \quad (\text{A1})$$

where  $Q_0(r)$  is a cubic polynomial of  $r$  and  $A = A_0 + A_1\mu + \dots$ , where

$$A_0 = \frac{\kappa}{\rho} = -Q_0(\sigma), \\ A_1 = \frac{1}{\rho} (\kappa\sigma - 1) + \int_0^\sigma dr Q_0(r), \quad (\text{A2})$$

$$Q_0(r) = a_0 + a_1 r + a_2 r^2 + a_3 r^3,$$

with

$$a_0 = \frac{4\eta - 1}{6\eta(\eta - 1)} \pi \sigma^2 + \frac{\pi \sigma^2}{6\eta} \frac{\mathcal{R}}{\eta - 1}, \\ a_1 = \frac{\pi \sigma^2 \kappa}{6\eta} (\eta - 1) + \frac{\pi \sigma}{6\eta} \frac{-10\eta^2 + 2\eta - 1}{(1 - \eta)^2} \\ + \frac{\pi \sigma}{6\eta} \frac{1 - 4\eta}{(1 - \eta)^2} \mathcal{R}, \quad (\text{A3}) \\ a_2 = \frac{\pi}{2} \frac{1 + 2\eta}{(1 - \eta)^2} - \frac{\pi \kappa \sigma}{2} + \frac{\pi}{2} \frac{\mathcal{R}}{(1 - \eta)^2}, \\ a_3 = \frac{\kappa \pi}{3}, \\ \mathcal{R} = [(1 + 2\eta)^2 + 2\kappa\sigma(1 - \eta)^3]^{1/2}.$$

Therefore, we have

$$\rho \int_0^\sigma dr Q_0(r) = 1 - \frac{\kappa\sigma}{2} - \frac{1 + 2\eta}{2(1 - \eta)^2} \left(1 + \frac{\mathcal{R}}{1 + 2\eta}\right). \quad (\text{A4})$$

The Laplace transform  $Q(s) = \int_0^\infty \exp(-sr) Q(r) dr$  is given by

$$1 - \rho Q(s) = \frac{S(s\sigma) + \exp(-s\sigma) L(s\sigma)}{(1 - \eta)^2 (s\sigma)^4}, \quad (\text{A5})$$

with

$$S(t) = (1 - \eta)^2 t^4 + (1 - \eta)(4\eta - 1 + \mathcal{R}) t^3 - [(-10\eta^2 + 2\eta - 1) \\ + (\eta - 1)^3 \kappa\sigma + (1 - 4\eta)\mathcal{R}] t^2 - 6\eta[1 + 2\eta - \kappa\sigma(1 - \eta)^2 \\ + \mathcal{R}] t - 12\eta(1 - \eta)^2 \kappa\sigma, \quad (\text{A6})$$

$$L(t) = [2\eta^2 + 8\eta - 1 - \kappa\sigma(1 - \eta)^3 + (1 + 2\eta)\mathcal{R}] t^2 \\ + 6\eta[1 + 2\eta + (1 - \eta)^2 \kappa\sigma + \mathcal{R}] t + 12\eta(1 - \eta)^2 \kappa\sigma.$$

When  $s \rightarrow 0$  we can expand  $Q(s)$

$$\rho Q(s) = -\frac{\kappa}{s} - \left[ \frac{-\eta^2 + 3\eta - 1/2}{(1 - \eta)^2} - \frac{\kappa\sigma}{2} + \frac{\mathcal{R}}{2(1 - \eta)^2} \right] \\ + s\sigma \left[ \frac{-2\eta^2 + 13\eta - 2}{12(1 - \eta)^2} + \frac{\kappa\sigma}{6} \left( \frac{\eta}{10} - 1 \right) \right. \\ \left. + \frac{2 + \eta}{12(1 - \eta)^2} \mathcal{R} \right] + O(s^2). \quad (\text{A7})$$

## APPENDIX B

For a background profile defined by Eq. (2.22), the formulas (2.15), (2.19), and (2.21) become

$$g(s) = \frac{1 + \frac{\kappa}{s} - \rho \int_0^\sigma Q_0(r) dr - \kappa(a + \sigma) + \frac{\kappa^2 s \exp(\alpha a)}{2\alpha^2(s + \alpha)[1 - \rho Q(s = \alpha)]}}{s[1 - \rho Q(s)]}, \quad (\text{B1})$$

$$g(o) = g(o) + \frac{\kappa^2}{2\alpha^2} \frac{\exp(\alpha a)}{1 - \rho Q(s = \alpha)}, \quad (\text{B2})$$

where  $g(o)_{\alpha \rightarrow \infty}$  is given by Eq. (2.19).

$$\beta Ze \Delta\psi = \beta Ze \Delta\psi + \frac{\kappa^2}{2\alpha^2} \frac{\exp(\alpha a)}{1 - \rho Q(s = \alpha)}, \quad (\text{B3})$$

where  $\Delta\psi_{\alpha \rightarrow \infty}$  is given by Eq. (2.21).

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