

# The ideally polarizable interface: Integral equations

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The integral equations used in the microscopic theory of the electric double layer are extended to the case of an impermeable interface separating two conducting media (ionic solutions or plasma). This system is a model for an ideally polarizable interface. Exact relations are given for the contact values of the one particle density function, and also for the pair correlation functions. We solve numerically the Poisson–Boltzmann (PB), the hypernetted chain (HNC), and mean spherical (MSA) approximations, and compare the results to the exact solution of the one component plasma in two dimensions.

## I. INTRODUCTION

In previous work,<sup>1</sup> we discussed the difference between the nonpolarizable interface, in which some of the charge carriers, ions or electrons, can cross the interface,<sup>2,3</sup> and the ideally polarizable interface (IPI), in which no carrier can cross the interface. The fact that the IPI must be ideally impermeable<sup>4,5</sup> was illustrated by a model of two interacting conducting media separated by a membrane of zero width. The equilibrium statistical mechanics was solved exactly in the special case of two classical one-component plasmas (OCP) in two dimensions at the reduced temperature 2.<sup>1</sup> Although the OCP–OCP interface is not a realistic description of the metal–electrolyte interface or of the interface between two electrolyte solutions (ITIES), the behavior of this model exhibits a remarkable resemblance to that of real systems. For instance, the natural external variable is the total potential drop across the interface and other quantities such as the surface excess charge are given as functions of the potential drop. This is close to the actual laboratory situation, where the potential is externally controlled, and the charge is not measured directly, but computed from other measurements, such as the capacitance or the surface tension.

The most interesting feature of our treatment is that we deal with the statistical mechanics of both sides of the interface and take into consideration the conducting nature of both media (see also Ref. 6). We must remark on the contrary that in much of the theoretical work on the metal–electrolyte interface, the metallic nature of the electrode is neglected or approximately described by boundary conditions (image forces) which, moreover, are not treated exactly. This is the case for the Gouy–Chapman theory<sup>7,8</sup> and for the more recent treatments using the Born–Green–Yvon (BGY), hypernetted chain (HNC), and modified Poisson–Boltzmann (MPB) integral equations.<sup>9</sup>

The purpose of the present work is to extend these integral equations used in the electrical double layer theory to our model of the IPI. The basic feature of our equations is that the fugacity of every component is not necessarily the same on both sides of the interface. We showed in Ref. 1 that the existence of an impermeable membrane permits us to fix different values for the fugacity on both sides and produces the characteristic surface charge potential drop curve of the IPI. We must remark that there is a subtle difference between the screening behavior of polarizable and nonpolarizable interfaces that is not at all present in previous theoretical discussions. In both cases the two-body correlations have a fast decay in the direction parallel to the interface, in accordance with Jancovici's conjecture<sup>3</sup> concerning the correlations at the interface between two conducting media. They obey the perfect screening theorems<sup>10–12</sup> concerning the nonexistence of multipoles, that is, any finite sized fixed multipole will be perfectly screened. But in the nonpolarizable interface where all charge carriers are free to move everywhere, even an infinite distribution of fixed charges, as for instance a charged plane or a layer of solvent dipoles, will be totally screened out by the mobile charges and give no contribution to the total potential drop and the capacitance. This surprising behavior is discussed in detail in Ref. 2 using as an example the exactly solvable two-dimensional one-component plasma. This is not true for the impermeable interface and the potential drop and the surface charge are not independent quantities any more.

Our basic approach is to write a separate equation for the one-particle density function, valid for each side of the interface. The solution of these equations is subject to a boundary condition at the membrane which is derived in Sec. II. We then get a closed system of equations. However, because of fluctuations induced by correlations between particles on different sides of the interface, the equations for the right and left sides are coupled to each other. Only in the mean field approximation<sup>1</sup> will they be decoupled.

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In Sec. III we will discuss two types of equations: those derived from the BGY equation, which are dynamic equations derived from force balance, and those derived from OZ (Ornstein-Zernike) type equations, derived basically from fluctuation theory. We apply these equations to the OCP-OCP interface model and in the last section, in the case of a uniform background, we show under which conditions the HNC, MSA (mean spherical) or PB (Poisson-Boltzmann) approximations are valid.

## II. DISCONTINUITY RELATION FOR THE ONE-PARTICLE DENSITY FUNCTION

Consider a mixture of ions of different charges  $e_i$ , sizes  $d_i$ , and concentrations  $\rho_i^{L,R}$  in a background of constant charge density  $-\alpha^{L,R}$  (Fig. 1). The labels  $L, R$  indicate the left or right side of the impermeable membrane located at  $x = 0$  (see Fig. 1). In this model the background is discontinuous across the membrane. This is not a necessary feature in our treatment but only a convenient one since we could also treat the case of a smoothly varying background.<sup>13</sup> Consider now the one-particle density function  $\rho_i(x)$ . We expect this function to be discontinuous across the membrane and we wish to find the magnitude of this discontinuity. Once this is done, we can solve the appropriate coupled equations for each side of the interface in the field of the other side.

The expansion for  $\rho_i^{L,R}(x)$ <sup>14-16</sup> is

$$\rho_i^{L,R}(x) = z_i^{L,R} \exp\left(-\beta u_i(x) + \frac{1}{2} \begin{array}{c} \bullet \\ \circ \end{array} + \frac{1}{2} \begin{array}{c} \bullet \\ \circ \\ \bullet \end{array} + \dots\right). \quad (1)$$

The fugacities  $z_i^L$  and  $z_i^R$  are defined by

$$z_i^{L,R} = \exp[\beta(\mu_i^{L,R} + e_i \varphi^{L,R})], \quad (2)$$

where  $\mu_i^L$  and  $\mu_i^R$  are the bulk chemical potentials and  $\varphi$  is the electric potential at infinity.  $\beta = 1/k_B t$  is the usual Boltzmann thermal factor.  $u_i(x)$  is the single particle potential which takes into account the existence of the impermeable membrane

$$u_i(x) = u_i^0(x) + u_i^s(x), \quad (3)$$

where  $u_i^0(x)$  is the infinitely repulsive part of the potential (see Eq. 5.21 of Ref. 1).  $u_i^s$  may be some non-Coulombic adsorption potential.

In Eq. (1) the field points are  $\sum_i \int dr \rho_i(r)$ , the bonds are  $f_{ij}(r) = \exp[-\beta u_{ij}(r)] - 1$  where  $u_{ij}$  is the pair potential.  $h_{ij}(r)$  and higher order functions are the correlation functions of the inhomogeneous system.<sup>17</sup> For a planar interface the first diagram is

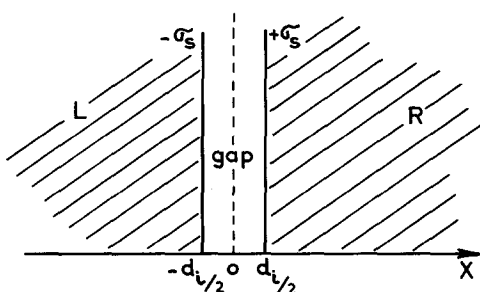


FIG. 1. System's geometry.

$$\begin{aligned} \begin{array}{c} \bullet \\ \circ \end{array} &= \sum_{i,j} \int dx_z \rho_j(x_z) J_{ij}(|x_1 - x_2|), \\ J_{ij}(|x_1 - x_2|) &= \int_0^{2\pi} d\phi \int_0^\infty dR_{12} R_{12} f_{ij}(r_{12}). \end{aligned} \quad (4)$$

Clearly  $J_{ij}(|x_1 - x_2|)$  is a continuous function and  $\rho_i(x)$  has a finite discontinuity across the interface. It can be shown that a similar argument holds for the higher order graphs. Therefore, at  $x = 0$  we get

$$\begin{aligned} \rho_i^L(0) \exp\{-\beta[\mu_i^L + e_i \varphi^L - u_i^L(0)]\} \\ = \rho_i^R(0) \exp\{-\beta[\mu_i^R + e_i \varphi^R - u_i^R(0)]\} \end{aligned} \quad (5)$$

which is the continuity condition for the one-particle direct correlation function<sup>18</sup>

$$c_i^{L,R}(1) = \beta u_i^{L,R}(1) + \ln[\rho_i^{L,R}(1)/z_i^{L,R}]. \quad (6)$$

Relation (5) is in general, not restricted to zero-size ions.

However, in the case of charged hard spheres ( $d_i \neq 0$ ) and rigid interfaces it is only a condition for the function  $y_i^{L,R}(x) = \rho_i^{L,R}(x) \exp[\beta u_i^{L,R}(x)]$  which remains finite throughout the interface.<sup>1</sup> We will discuss this problem in a future application of the present work. In order to get a relation for the contact density we must use approximations: the simplest of these approximations consists of adding to the potential drop a contribution due to the field in the gap separating the two phases:

$$\begin{aligned} \rho_i^L(-d_i/2)/\rho_i^R(d_i/2) \\ = \exp\{-\beta[\mu_i^R - \mu_i^L + e_i(\varphi^R - \varphi^L) - e_i 4\pi\sigma_s d_i]\}, \end{aligned} \quad (7)$$

where  $d_i$  is the width of the gap separating the two sides of the system (Fig. 1) and  $\sigma_s$ , the excess charge defined by

$$\sigma_s = \int_0^\infty dx [q(x) - \alpha^R] = - \int_{-\infty}^0 dx [q(x) - \alpha^L] \quad (8)$$

where

$$q(x) = \sum_i e_i \rho_i(x).$$

In Eq. (7) and in the rest of this paper we assume for the sake of simplicity that  $u_i^s(x) = 0$ .

Relation (7) is really a mean field approximation, similar to that of Ref. 1. When  $d_i = 0$ , or equivalently the ions are point charges and can approach the interface from both sides infinitely close, then

$$\rho_i^L(0)/\rho_i^R(0) = z_0^i, \quad (9)$$

where

$$z_0^i = \exp[\beta(\mu_i^L - \mu_i^R - e_i \Delta\phi)]$$

and

$$\Delta\phi = \varphi^R - \varphi^L,$$

which is an exact relation in any dimensionality, but has been proven to be true for the two-dimensional OCP at reduced temperature 2.<sup>1</sup>

## III. DYNAMIC EQUATIONS

### A. The BGY equation

The BGY equation for the left and right side of the membrane can be written in the form<sup>19</sup>:

$$\begin{aligned}
-k_B T \nabla \rho_i(1) &= e_i \rho_i(1) \nabla \varphi(1) \\
&+ \sum_j \int d^2 \rho_{ij}^T(1,2) \nabla w_{ij}(1,2) \\
&+ \sum_j \int d^2 \rho_{ij}(1,2) \nabla u_{ij}^0(1,2), \quad (10)
\end{aligned}$$

where  $\rho_i(1)$  is the one-body density.  $\rho_{ij}(1,2)$  is the two-body density. Furthermore, the truncated two-body density is

$$\rho_{ij}^T(1,2) = \rho_{ij}(1,2) - \rho_i(1)\rho_j(2). \quad (11)$$

$w_{ij}(1,2)$  is the Coulomb potential,  $u_{ij}^0(1,2)$  is the short range potential and  $\varphi(1)$  is the local electrostatic potential which satisfies the Poisson equation

$$\begin{aligned}
\frac{\partial^2 \varphi(1)}{\partial x_1^2} &= -4\pi [q(x_1) - \alpha^{L,R}] \\
(2\pi \text{ for two dimensions}). \quad (12)
\end{aligned}$$

If the ions are of finite size, then the distance of closest approach is  $d_i/2$ , and Eq. (10) is valid for  $x > d_i/2$  (right side) or  $x < -d_i/2$  (left side).

Quantities of electrochemical interest are the excess charge density on each side of the interface [Eq. (8)] and the differential capacitance of the system

$$C_d = \partial \sigma_s / \partial \Delta \varphi. \quad (13)$$

The following contact theorem was proven in Ref. 1 for the OCP-OCP interface:

$$\begin{aligned}
P^L - P^R &= [\alpha^L - \alpha^R] [\varphi(0) - \frac{1}{2}(\varphi^L + \varphi^R)] \\
&+ \frac{1}{2}[\alpha^L + \alpha^R] \Delta \varphi + k_B T \sum_i [\rho_i^L(0) - \rho_i^R(0)], \quad (14)
\end{aligned}$$

where  $P^L$  and  $P^R$  are the bulk pressures on both sides of the interface. We will show that Eq. (10) yields exactly the same theorem with the bulk pressure of the approximation used to calculate the pair correlation function. This can be done by simple integration.<sup>19-21</sup> Let us first integrate Eq. (10) from  $-d_i/2$  to a point  $-x_b$ , deep inside the bulk phase L:

$$\begin{aligned}
k_B T \sum_i [\rho_i^L - \rho_i^L(-d_i/2)] \\
= - \int_0^{-x_b} dx_1 q(x_1) \frac{\partial \varphi(x_1)}{\partial x_1} - \int_0^{-x_b} dx_1 \int d^2 \\
\times \left[ \sum_{i,j} \rho_{ij}^T(1,2) \frac{\partial w_{ij}(r_{12})}{\partial x_2} + \rho_{ij}(1,2) \frac{\partial u_{ij}^0(r_{12})}{\partial x_2} \right]. \quad (15)
\end{aligned}$$

Here we have used the fact that  $\rho_i(x) = 0$  for  $x_i > -d_i/2$ . The first term of the right hand side yields

$$\int_0^{-x_b} dx_1 q(x_1) \frac{\partial \varphi(x_1)}{\partial x_1} = \alpha^L [\varphi^L - \varphi(0)] + \frac{1}{8\pi} E^2(0), \quad (16)$$

where we have used the Poisson equation (12) and  $E(-\infty) = 0$  [ $E(x)$  is the local electrostatic field]. Now we integrate Eq. (10) from  $d_i/2$  to  $x_b$  and sum over  $i$ :

$$k_B T \sum_i [\rho_i^R - \rho_i^R(d_i/2)]$$

$$\begin{aligned}
&= -\alpha^R [\varphi^R - \varphi(0)] + \frac{1}{8\pi} E^2(0) - \int_0^{+x_b} dx_1 \int d^2 \\
&\times \left[ \sum_{i,j} \rho_{ij}^T(1,2) \frac{\partial w_{ij}(r_{12})}{\partial x_2} + \rho_{ij}(1,2) \frac{\partial u_{ij}^0(r_{12})}{\partial x_2} \right]. \quad (17)
\end{aligned}$$

Subtracting Eq. (17) from Eq. (15) we get

$$\begin{aligned}
k_B T \sum_i [\rho_i^L - \rho_i^R] - \int_{-x_b}^{+x_b} dx_1 \int d^2 \\
\times \left[ \sum_{i,j} \rho_{ij}^T(1,2) \frac{\partial w_{ij}(r_{12})}{\partial x_2} + \rho_{ij}(1,2) \frac{\partial u_{ij}^0(r_{12})}{\partial x_2} \right] \\
= \alpha^L [\varphi(0) - \varphi^L] - \alpha^R [\varphi(0) - \varphi^R] \\
+ k_B T \sum_i \left[ \rho_i^L \left( -\frac{d_i}{2} \right) - \rho_i^R \left( \frac{d_i}{2} \right) \right]. \quad (18)
\end{aligned}$$

The integral in the right-hand side of Eq. (18) can be written

$$\begin{aligned}
\sum_{i,j} \int_{-x_b}^{+x_b} dx_1 \int d^2 \Rightarrow \\
-2\pi \sum_{i,j} \int_{-x_b}^{+x_b} dx_1 \left[ \int_{-\infty}^{-x_b} dx_2 + \int_{-x_b}^{+x_b} dx_2 + \int_{+x_b}^{\infty} dx_2 \right] x_{12} \\
\times \int_{|x_{12}|}^{\infty} dr_{12} [\rho_{ij}^T(1,2) w'_{ij}(r_{12}) + \rho_{ij}(1,2) u'_{ij}(r_{12})]. \quad (19)
\end{aligned}$$

The integrand is antisymmetric and therefore the middle integral is zero. Since we are arbitrarily far away from the interface we can replace  $\rho_{ij}(1,2)$  by its bulk value. After some simple transformations we see that the integral is the one in the expression of the virial pressure:

$$\begin{aligned}
P^{L,R} &= k_B T \sum_i \rho_i^{L,R} - \frac{1}{6} \sum_{ij} \int d^2 \\
&\times \left[ \rho_{ij}^T(r_{12}) \frac{\partial w_{ij}(r_{12})}{\partial \mathbf{r}_{12}} \cdot \mathbf{r}_{12} + \rho_{ij}(r_{12}) \frac{\partial u_{ij}(r_{12})}{\partial \mathbf{r}_{12}} \cdot \mathbf{r}_{12} \right], \quad (20)
\end{aligned}$$

where  $\rho_{ij}(r_{12})$  is the homogeneous density pair correlation function. From here we get

$$\begin{aligned}
P^L - P^R &= \alpha^L [\varphi(0) - \varphi^L] - \alpha^R [\varphi(0) - \varphi^R] \\
&+ k_B T \sum_i [\rho_i^L(-d_i/2) - \rho_i^R(d_i/2)]. \quad (21)
\end{aligned}$$

For  $d_i = 0$  we recover Eq. (14) which is the contact theorem for point ions.

Combining these expressions with the discontinuity relation (9) we get some interesting sum rules for the pair inhomogeneous correlation function: Dividing both sides of Eq. (10) by  $\rho_i(1)$  and then integrating from  $-x_b$  to 0 and 0 to  $x_b$ , we see that

$$\begin{aligned}
k_B T \ln [g_i^L(0)/g_i^R(0)] \\
= -e_i \Delta \varphi - \sum_j \int_{-x_b}^{+x_b} dx_1 \frac{1}{\rho_i(x_1)} \int d^2 \\
\times [\rho_{ij}^T(1,2) w'_{ij}(r_{12}) + \rho_{ij}(1,2) u'_{ij}(r_{12})] \quad (22)
\end{aligned}$$

with  $g_i(1) = \rho_i(1)/\rho_i$  so that

$$\begin{aligned}
k_B T \ln [g_i^L(0)/g_i^R(0)] \\
= -e_i \Delta \varphi + P_i^L/\rho_i^L - P_i^R/\rho_i^R + I_i \quad (23)
\end{aligned}$$

with

$$P_i^{L,R} = \rho_i^{L,R} k_B T - \frac{1}{6} \sum_j \int d^2 \times \left[ \rho_{ij}^T(r_{12}) \frac{\partial w_{ij}(r_{12})}{\partial \mathbf{r}_{12}} \cdot \mathbf{r}_{12} + \rho_{ij}(r_{12}) \frac{\partial u_{ij}^0(r_{12})}{\partial \mathbf{r}_{12}} \cdot \mathbf{r}_{12} \right],$$

$$I_i = 2\pi \int dx_1 dx_2 \sum_j \rho_j(x_2) x_{12} \int_{|x_{12}|}^{\infty} dr_{12} \times [h_{ij}(1,2) w'_{ij}(r_{12}) + g_{ij}(1,2) u'_{ij}(r_{12})]$$

and

$$g_{ij}(1,2) = \rho_{ij}(1,2)/\rho_i(1)\rho_j(2); \quad h_{ij} = g_{ij} - 1.$$

If Eq. (9) holds, then this is equivalent to

$$\mu_i^L - \mu_i^R = k_B T \ln[\rho_i^L/\rho_i^R] + P_i^L/\rho_i^L - P_i^R/\rho_i^R + I_i. \quad (24)$$

This equation expresses the force balance across the interface.<sup>19,20</sup> If the bulk densities are the same on both sides then Eqs. (9) and (24) imply

$$I_i = 0. \quad (25)$$

Finally we remark that the contact theorem (24) takes a particularly simple form when the background density is zero (ITIES):

$$P^L - P^R = k_B T \sum_i [\rho_i^L(-d_i/2) - \rho_i^R(d_i/2)]. \quad (26)$$

The interesting feature is that in this equation the electrostatic Maxwell tensor term of the single wall case<sup>21,22</sup> has disappeared.

**B. The WLMB equation**

From the dynamic BGY hierarchy of equations we can derive the Wertheim-Lovett-Mou-Buff equations (WLMB).<sup>18,23</sup> For systems with long range forces we have<sup>12</sup>:

$$\frac{\partial \rho_i(1)}{\partial x_1} = -\beta e_i \rho_i(1) \frac{\partial \varphi(1)}{\partial x_1} - \rho_i(1) \sum_j \int d^2 \rho_j(x_2) \frac{\partial}{\partial x_2} C_{ij}^0(1,2), \quad (27)$$

where  $C_{ij}^0(1,2)$  is the short ranged part of the inhomogeneous direct correlation function

$$C_{ij}^0(1,2) = C_{ij}(1,2) + \beta \omega_{ij}(r_{12}). \quad (28)$$

This equation must be solved for the left and right sides separately, subject to the jump condition [Eqs. (5), (7), and (9)]. By a calculation analogous to that of the previous section we can derive a sum rule for the unknown  $C_{ij}^0(1,2)$ :

$$\beta [P^L - P^R] = \sum_i (\rho_i^L - \rho_i^R) - \sum_{i,j} \int dx_1 \rho_i(x_1) \times \int d^2 \rho_j(x_2) \frac{\partial}{\partial x_2} C_{ij}^0(1,2), \quad (29)$$

where we used Eq. (21). If relation (9) holds then we get also

$$\beta (\mu_i^L - \mu_i^R) = \ln[\rho_i^L/\rho_i^R] - \sum_j \int dx_1 dx_2 \rho_j(x_2) \int d \mathbf{R}_{12} \frac{\partial}{\partial x_2} C_{ij}^0(1,2), \quad (30)$$

$$\mathbf{r}_{12} = \{x_{12}, \mathbf{R}_{12}\},$$

which for equal bulk densities implies

$$\sum_j \int dx_1 dx_2 \rho_j(x_2) \int d \mathbf{R}_{12} \frac{\partial}{\partial x_2} C_{ij}^0(1,2) = 0. \quad (31)$$

The WLMB equation is an exact equation but contains the unknown function  $C_{ij}^0(1,2)$ . For systems with uniform background we may simply replace this function by the bulk direct correlation function, and because of the fact that Eq. (31) is automatically satisfied, get quite a good approximation. Unfortunately this is not true for the general case of a discontinuous interface.

**C. The Poisson-Boltzmann approximation (PB)**

The simplest approximation is to ignore the effect of the pair correlations. Then we get the PB (GC) equation:

$$\nabla^2 \tilde{\varphi}(x) = -\kappa_{L,R}^2 \sum_i z_i v_i^{L,R} [e^{-z_i \tilde{\varphi}(x)} - 1], \quad (32)$$

where

$$\tilde{\varphi}(x) = \beta e \varphi(x)$$

$$\kappa_{L,R}^2 = 4\pi \beta e^2 \rho_0^{L,R}$$

$$v_i^{L,R} = \rho_i^{L,R}/\rho_0^{L,R} \quad \rho_0^{L,R} = \sum \rho_i^{L,R}$$

$$z_i = e_i/e.$$

$\kappa_{L,R}$  is the inverse Debye length and  $e$  is the elementary charge. This equation can be integrated using the standard trick of multiplying by  $2\partial\tilde{\varphi}/\partial x$ ;

$$\frac{\partial}{\partial x} \left[ \frac{\partial \tilde{\varphi}(x)}{\partial x} \right]^2 = 2\kappa_{L,R}^2 \frac{\partial}{\partial x} \sum_i v_i [e^{-z_i \tilde{\varphi}(x)} + z_i \tilde{\varphi}(x)] \Big|_{L,R}. \quad (33)$$

Integrating between  $x$  and  $\infty$  in the right side, and  $-\infty$  to  $x$  in the left side we obtain

$$\left[ \frac{\partial \tilde{\varphi}(x)}{\partial x} \right]_{L,R}^2 = 2\kappa_{L,R}^2 \sum_i v_i^{L,R} \{ e^{-z_i [\tilde{\varphi}(x) - \tilde{\varphi}^{L,R}]} + z_i [\tilde{\varphi}(x) - \tilde{\varphi}^{L,R}] - 1 \}. \quad (34)$$

For the OCP-OCP interface, we get

$$-\beta e E(x) = \frac{\partial \tilde{\varphi}(x)}{\partial x} = \pm \sqrt{2} \begin{cases} \kappa_L [e^{-[\tilde{\varphi}(x) - \tilde{\varphi}^L]} + \tilde{\varphi}(x) - \tilde{\varphi}^L - 1]^{1/2} & x < 0 \\ \kappa_R [e^{-[\tilde{\varphi}(x) - \tilde{\varphi}^R]} + \tilde{\varphi}(x) - \tilde{\varphi}^R - 1]^{1/2} & x > 0 \end{cases} \quad (35)$$

The charge conservation condition

$$E(0) = -4\pi \cdot \sigma_s \quad (2\pi \cdot \sigma_s \text{ in 2 dimensions}) \quad (36)$$

yields, together with Eq. (35) the set of equations

$$|\sigma_s| = \sqrt{2} e \rho^L / \kappa_L [e^{-u} + u - 1]^{1/2}, \quad (37)$$

$$|\sigma_s| = \sqrt{2} e \rho^R / \kappa_R [e^{-u + \Delta\tilde{\varphi}} + u - \Delta\tilde{\varphi} - 1]^{1/2}, \quad (38)$$

where  $u = \tilde{\varphi}(0) - \tilde{\varphi}^L$  and  $\Delta\tilde{\varphi} = \beta e \Delta\varphi$ .

We can establish, then, a relation between the quantities  $u$  and  $\Delta\tilde{\varphi}$  for this model:

$$e^{-u} [m^2 - e^{\Delta\tilde{\varphi}}] + (u - 1)(m^2 - 1) + \Delta\tilde{\varphi} = 0, \quad (39)$$

where

$$m^2 = \alpha^L / \alpha^R. \quad (40)$$

We observe that this equation is merely the contact theorem (14) with the ideal gas pressures  $P^{L,R} = \rho^{L,R} k_B T$ .

Clearly the contact densities are

$$\rho^L(0) = \rho^L e^{-u} \tag{41}$$

$$\rho^R(0) = \rho^R e^{-u + \Delta\tilde{\varphi}}, \tag{42}$$

which shows that for the OCP–OCP model the jump condition (9) is not satisfied, except when  $m = 1$ .

The asymptotic behavior of the PB approximation for large  $\Delta\tilde{\varphi}$  and for small  $\Delta\tilde{\varphi}$  is easily obtained. For small  $\Delta\tilde{\varphi}$

$$\tilde{\varphi}(x) = \frac{\Delta\tilde{\varphi}}{1+m} e^{\kappa_L x} + \tilde{\varphi}^L \quad (x < 0), \tag{43}$$

$$\tilde{\varphi}(x) = -\frac{m\Delta\tilde{\varphi}}{1+m} e^{-\kappa_R x} + \tilde{\varphi}^R \quad (x > 0), \tag{44}$$

and

$$\beta e \sigma_s = \frac{\kappa_L}{4\pi(1+m)} \Delta\tilde{\varphi} \quad (1/2\pi \text{ in two dimensions}). \tag{45}$$

This gives for the differential capacity at the point of zero charge

$$C_D = \kappa_L / 4\pi(1+m). \tag{46}$$

Notice that in the exact solution for the 2D case<sup>1</sup> the potential at the point of zero charge is zero only if the background is uniform. For large  $\Delta\tilde{\varphi}$  we find

$$\begin{aligned} \sigma_s &\sim \sqrt{2e\rho^L} / (\kappa_L \sqrt{\Delta\tilde{\varphi}}) \quad (\Delta\tilde{\varphi} > 0), \\ \sigma_s &\sim -\sqrt{2e\rho^L} / (\kappa_L m \sqrt{-\Delta\tilde{\varphi}}) \quad (\Delta\tilde{\varphi} < 0). \end{aligned} \tag{47}$$

( $\sigma_s$  and  $\Delta\tilde{\varphi}$  are of the same sign.) This yields

$$\begin{aligned} C_D &\sim \beta e^2 \rho^L / (\kappa_L \sqrt{2\Delta\tilde{\varphi}}) \quad (\Delta\tilde{\varphi} > 0), \\ C_D &\sim \beta e^2 \rho^L / (\kappa_L m \sqrt{-2\Delta\tilde{\varphi}}) \quad (\Delta\tilde{\varphi} < 0), \end{aligned} \tag{48}$$

which we believe is the correct asymptotic behavior of the capacity.

#### IV. HNC AND MSA FOR UNIFORM BACKGROUND OCP–OCP

Assume that  $c_0(\mathbf{r}_1, \mathbf{r}_2) = c_0(r_{12})$  in the WLMB equation (27). After integrating we obtain the HNC closure of the Ornstein–Zernike (OZ) equation

$$\ln[1 + h(x)] = \kappa(x) - \begin{cases} \tilde{\varphi}(x) - \tilde{\varphi}^L & (x < 0) \\ \tilde{\varphi}(x) - \tilde{\varphi}^R & (x > 0) \end{cases} \tag{49}$$

where

$$\begin{aligned} \kappa(x) &= \rho \int d\mathbf{r}_2 C_0(r_{12}) h(x_2), \\ &= \rho(x) = \rho[h(x) + 1]. \end{aligned} \tag{50}$$

If  $h(x)$  is small then we can linearize the logarithm of the left-hand side. This yields the MSA, which, clearly, is valid only for small values of the potential drop.

##### A. Linear regime: The MSA equation

When  $\Delta\tilde{\varphi} = 0$  and the background is uniform the system acts as if there were no impermeable membrane. This is so because we are dealing with point charges, and in this case there are no position dependent forces acting on them. This

means that  $\rho(x) = \text{constant}$ . Hence for small  $\Delta\varphi$ ,  $c_0(\mathbf{r}_1, \mathbf{r}_2) \sim c_0(r_{12})$  even in the vicinity of the interface. We conjecture that for the uniform background case the MSA is asymptotically exact. Although we lack a general proof of this statement, we show in the Appendix that this conjecture is true for the exactly solvable case in two dimensions.

The MSA can be readily solved by Fourier transformation. We find

$$\hat{h}(k) = -\Delta\tilde{\varphi} / ik [1 - \rho\hat{c}(k)], \tag{51}$$

where

$$\hat{h}(k) = \int_{-\infty}^{\infty} dx e^{ikx} h(x) \tag{52}$$

and

$$\hat{c}(k) = \int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} c(r); \tag{53}$$

hence

$$h(x) = -\frac{\Delta\tilde{\varphi}}{2\pi i} \int_{-\infty + i\delta}^{\infty + i\delta} dk \frac{e^{-ikx}}{k [1 - \rho\hat{c}(k)]} \tag{54}$$

with  $\delta > 0$ .

Since  $\kappa(x)$  is continuous for  $x = 0$ , we have

$$h^R(0) - h^L(0) = \Delta\tilde{\varphi}. \tag{55}$$

From Eq. (54) we find that

$$h(-x) = -h(x) \tag{56}$$

and therefore

$$h^L(0) = -h^R(0) = \frac{1}{2} \Delta\tilde{\varphi} \tag{57}$$

so that the jump condition (9) is satisfied in the linear regime  $z_0 = 1 - \Delta\tilde{\varphi}$ .

We have also

$$\begin{aligned} e[\varphi(0) - \phi^L] &= 4\pi e^2 \rho \int_{-\infty}^0 dx x h(x) \\ &= 4\pi e^2 \rho \int_0^{\infty} dx x h(x) \\ &= -e[\varphi(0) - \varphi^R] = \frac{1}{2} e\Delta\varphi. \end{aligned} \tag{58}$$

Furthermore the contact theorem (14) is also satisfied in the linear approximation.

In the MSA the excess charge density, and therefore the differential capacity, are calculated in closed form;

$$\begin{aligned} \sigma_s &= \rho \int_0^{\infty} dx h(x) \\ &= \frac{\beta e \Delta\varphi}{\pi} \rho \int_0^{\infty} dk \frac{1}{k^2 [1 - \rho\hat{c}(k)]} \end{aligned} \tag{59}$$

and

$$c_D = \frac{\beta e^2}{\pi} \rho \int_0^{\infty} dk \frac{1}{k^2 [1 - \rho\hat{c}(k)]}. \tag{60}$$

In the 2D solvable model these are the exact values for  $\Delta\varphi = 0$ .

If we take  $\hat{c}_0(k) = 0$ , i.e.,  $\rho\hat{c}(k) = -\kappa^2/k^2$  then we recover the PB result Eq. (32).

**B. The HNC equation**

The HNC equation (49) can be solved numerically by an iterative procedure. It is also clear that for the uniform background case the jump condition (9) is also satisfied by the HNC. To insure electroneutrality during the numerical integration of the OZ equation, it is convenient to write the HNC equation in terms of the potential.<sup>24</sup>

Adding  $\partial^2 \tilde{\varphi}(x)/\partial x^2$  to both sides of Eq. (49), and regrouping the terms we get a second order differential equation

$$\begin{aligned} \kappa^2 [\ln[1 + h(x)] - \kappa(x) - h(x)] \\ = \frac{d^2 \tilde{\varphi}}{dx^2} - \beta e k^2 \begin{cases} \varphi(x) - \varphi^R & x > 0 \\ \varphi(x) - \varphi^L & x < 0 \end{cases} \\ \equiv T(x) \end{aligned} \tag{61}$$

which is integrated subject to the boundary conditions

$$\varphi^L(0) = \varphi^R(0), \tag{62}$$

$$\left. \frac{\partial \varphi}{\partial x} \right|_L = \left. \frac{\partial \varphi}{\partial x} \right|_R \quad (x = 0)$$

to yield

$$\begin{aligned} \varphi(x) = -\frac{1}{2\kappa} e^{-\kappa x} \int_{-\infty}^x dy e^{\kappa y} T(y) \\ - \frac{1}{2\kappa} e^{\kappa x} \int_x^{\infty} dy e^{-\kappa y} T(y) + \begin{cases} \varphi^R \left(1 - \frac{e^{-\kappa x}}{2}\right) & x > 0 \\ \varphi^R \frac{e^{\kappa x}}{2} - \varphi^L & x < 0 \end{cases} \end{aligned} \tag{63}$$

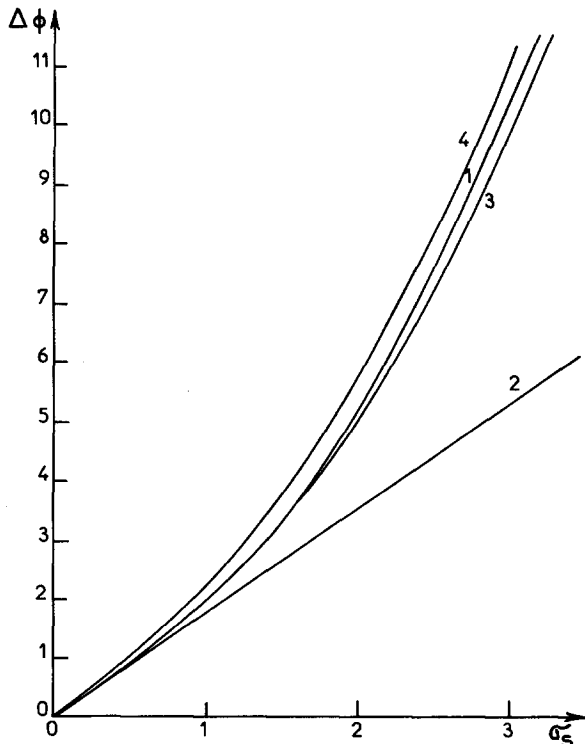


FIG. 2. Potential drop vs charge for the OCP-OCP model. For  $m = 1$ : (1) exact; (2) MSA; (3) HNC; (4) PB. Units are  $e = 1$ ;  $\rho = 1/\pi$

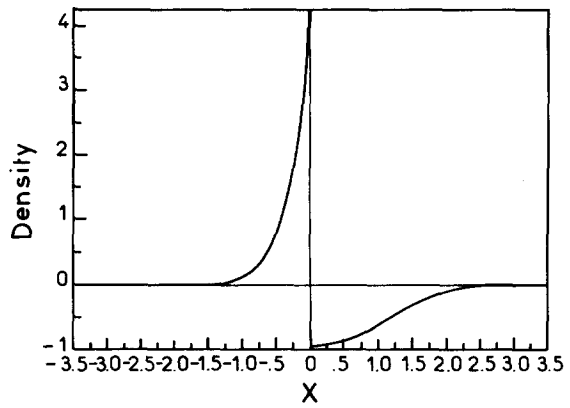


FIG. 3. Density profile for  $m = 1$  and  $\Delta\varphi = 5$  for the OCP-OCP model;  $h(x) = g(x) - 1$ .

As a test of the accuracy of this solution we have performed the numerical integration for the exactly solvable case in two dimensions: the comparison of the approximate theories to the exact result obtained in Ref. 1 for the charge  $\sigma_s$  as a function of the potential drop  $\Delta\varphi$  is shown in Fig. 2. The agreement is really good for large potential drop. In Fig. 3 we compare the density profiles  $h(x)$  of the HNC to the exact result for  $\Delta\varphi = 5$ : at the scale of the figure the results are indistinguishable from the exact values. The contact values are  $\rho_{\text{HNC}}^L(0) = 1.617$ ,  $\rho_{\text{EXACT}}^L(0) = 1.602$ ;  $\rho_{\text{HNC}}^R(0) = 1.173 \times 10^{-2}$ ,  $\rho_{\text{EXACT}}^R(0) = 1.080 \times 10^{-2}$ . For large potential drop the approximate and exact curves become parallel, which means that the slope (which is the differential capacitance) must be the same, and also equal to the result of the PB equation. The PB is really not a bad approximation, although it is certainly worst for low couplings.

Notice also that for the uniform background case Eq. (39) has the simple solution

$$u = \ln \left[ \frac{e^{\Delta\tilde{\varphi}} - 1}{\Delta\tilde{\varphi}} \right], \tag{64}$$

which yields

$$|\sigma_{\text{PB}}| = \sqrt{2} \frac{\rho}{\kappa} \left[ \frac{\Delta\tilde{\varphi}}{e^{\Delta\tilde{\varphi}} - 1} - \ln \left( \frac{\Delta\tilde{\varphi}}{e^{\Delta\tilde{\varphi}} - 1} \right) - 1 \right]^{1/2}. \tag{65}$$

It is amusing to note that the PB contact values are the exact ones for this case,<sup>1</sup>

$$\begin{aligned} \rho^L(0) &= \rho \frac{\Delta\tilde{\varphi}}{e^{\Delta\tilde{\varphi}} - 1} = \rho \frac{z_0}{z_0 - 1} \ln z_0, \\ \rho^R(0) &= \rho \frac{\Delta\tilde{\varphi}}{1 - e^{-\Delta\tilde{\varphi}}} = \rho \frac{1}{z_0 - 1} \ln z_0. \end{aligned} \tag{66}$$

**APPENDIX: THE EXACTLY SOLVABLE CASE IN THE LINEAR REGIME**

From Ref. 1 we know that the exact density for  $x > 0$  is

$$\rho(x) = \frac{2}{\pi^{3/2}} \int_{-\infty}^{\infty} dt \frac{e^{-(t+x\sqrt{2})^2}}{\text{erfc}(t) + z_0 \text{erfc}(-t)} \tag{A1}$$

where  $\text{erfc}(t)$  is the complementary error function and the density is  $\rho = 1/\pi$ . In the linear regime

$$z_0 = 1 - 2\Delta\varphi/e; \tag{A2}$$

hence

$$\begin{aligned}\rho(x) &= 1/\pi^{3/2} \int_{-\infty}^{\infty} dt e^{-(t+x\sqrt{2})^2} \left\{ 1 + \frac{\Delta\varphi}{e} \operatorname{erfc}(-t) \right\} \\ &= 1/\pi \left[ 1 + \frac{\Delta\varphi}{e} \operatorname{erfc}(x) \right].\end{aligned}\quad (\text{A3})$$

Similarly for  $x < 0$  we find

$$\rho(x) = 1/\pi [1 - \Delta\varphi/e \operatorname{erfc}(-x)]. \quad (\text{A4})$$

This gives for the Fourier transform of  $\hat{h}(x)$

$$\begin{aligned}\hat{h}(k) &= \frac{2\Delta\varphi}{e} i \int_0^{\infty} dx \operatorname{erfc}(x) \sin kx \\ &= -\frac{2\Delta\varphi}{e} (1 - e^{-k^2/4})/ik.\end{aligned}\quad (\text{A5})$$

But (Ref. 25),

$$\rho\hat{c}(k) = e^{-k^2/4}/(e^{-k^2/4} - 1) \quad (\text{A6})$$

so that

$$\hat{h}(k) = \frac{-2\Delta\varphi}{ik} \frac{1}{e^{-k^2/4} - 1} \quad (\text{A7})$$

which is the solution of the MSA equation (51).

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