A simple model for semipermeable membrane: Donnan equilibrium

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We study a model for macroions in an electrolyte solution confined by a semipermeable membrane. The membrane finite thickness is considered and both membrane surfaces are uniformly charged. The model explicitly includes electrostatic and size particles correlations. Our study is focused on the adsorption of macroions on the membrane surface and on the osmotic pressure. The theoretical prediction for the osmotic pressure shows a good agreement with experimental results.

Keywords: Donnan equilibrium, semipermeable membrane, charge reversal, charge inversion, adsorption, macroions.

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I. INTRODUCTION

Physics of two ionic solutions separated by a semipermeable membrane is of wide interest in cell biology and colloids science [1, 2, 3]. A thermodynamical study of this problem was first carried out by F. G. Donnan [4, 5], considering the two fluids phases (here referred as α and β) in the following way: (i) the α-phase contains two (small) ionic species, (ii) the β-phase contains the same ionic species as the α-phase plus one macroion species. The two fluid phases are separated by a membrane which is permeable to the small ions and impermeable to macroions, therefore, they interchange small ions whereas macroions are restricted to the β-phase. The permeability condition is imposed by assuming (in both phases) a constant chemical potential of the permeating species. In this simple model, Donnan derived an expression for the osmotic pressure (in terms of the ionic charge, concentration and excluded volume) which well describes systems close to ideality. Historically, this problem has been known as Donnan equilibrium. More recently some theories have been proposed to interpret osmotic pressure data [6, 7]. These theories consider phenomenologically the macroion-macroion and ion-macroion many-body interactions, and provide a better fit for the osmotic pressure of macroions solutions than Donnan theory.

The surface of a biological membrane has a net charge when it is in aqueous solution [1] thus, at a fluid-membrane interface a broad variety of phenomena occur. It is known that ionic solutions in the neighborhood of a charged surface produce an exponentially decaying charge distribution, known as the electrical double layer. Low-concentrated solutions of monovalent ions are well described by the Gouy-Chapman theory (Poisson-Boltzmann equation) [8, 9]. However, multivalent ions display important deviations from this picture [10] and more powerful theories from modern statistical mechanics (such as molecular simulation [11, 12, 13], density functionals [14, 15, 16] and integral equations [17, 18, 19, 20, 21]) have been implemented for studying ions adsorption and interfacial phenomena. Macroions adsorption is a subject of current interest: In molecular engineering, the macroions adsorption mechanisms are basic in self-assembling polyelectrolyte layers on a charged substrate [22] and novel colloids stabilization mechanisms [23].

By means of integral equations, a previous study of Donnan equilibrium has been carried out by Zhou and Stell [24, 25]. They used the method proposed by Henderson et al. [17], which can be described as follows: starting from a semipermeable spherical cavity [26], the planar membrane is obtained taking the limit of infinite cavity radius. Within this model, they obtained the charge distribution and mean electrostatic potential. However, due to the approximations used, they end up just with the integral version of the linear Poisson-Boltzmann equation. A general shortcoming of the Poisson-Boltzmann equation is that ionic size effects (short range correlations) are completely neglected, in consequence, the description of interfacial phenomena and computation of thermodynamical properties is limited and valid only for low values of charge and concentration.

From previous studies of two fluid phases separated by a permeable membrane, it is known that the adsorption phenomena are strongly influenced by the membrane thickness [27, 28, 29]. On the other hand, short range correlations influence effective colloid-colloid interaction [30, 31, 32, 33, 34]. thermodynamical properties [35] and adsorption phenomena [36, 37] in colloidal dispersions. From these antecedents it is seen that there are several relevant aspects not considered in previous studies of Donnan equilibrium which deserve a proper consideration. In this study we consider explicitly the following effects: many-body (short and long range) correlations, the membrane thickness and the surface charge densities on each of the membrane faces. We use simple model interactions and our study is carried out by means of integral equations. The theory gives the parti-
cles distribution in the neighborhood of the membrane, from which, the osmotic pressure is calculated. There are two points that we will address in this study: the adsorption of macroions at the membrane surface and the computation of the osmotic pressure for macroions solutions. Concerning the adsorption phenomena, we observe a broad variety of phenomena: charge reversal, charge inversion and macroions adsorption on a like-charged surface due to the fluid-fluid correlation. The computed osmotic pressure is compared with experimental results for a protein solution, obtaining an excellent agreement over a wide regime of concentrations.

The paper is organized as follows: In section II we describe the integral equations method and the membrane and fluid models. In the same section, we derive the hypernetted chain/mean spherical (HNC/MS) integral equations for the semipermeable membrane and the equations to compute the osmotic pressure. In section III a variety of results are discussed and finally in section IV some conclusions are presented.

II. THEORY

A. Integral equations for inhomogeneous fluids

The method that we use to derive integral equations for inhomogeneous fluids makes use of a simple fact: In a fluid, an external field can be considered as a particle in the fluid, i.e., as one more species infinitely dilute. This statement is valid in general, however, it is particularly useful in the statistical mechanics theory for inhomogeneous fluids described below.

The multi-component Ornstein-Zernike equation for a fluid made up of \(n+1\) species is

\[
h_{ij}(\mathbf{r}_2) = c_{ij}(\mathbf{r}_2) + \sum_{m=1}^{n+1} \rho_m \int h_{im}(\mathbf{r}_{23})c_{mj}(\mathbf{r}_{13}) \, dv_3,
\]

(1)

where \(\rho_m\) is the number density of species \(m\), \(h_{ij}(\mathbf{r}_2)\) is the total direct correlation function for two particles at \(\mathbf{r}_2\) and \(\mathbf{r}_1\) of species \(i\) and \(j\), respectively; with \(g_{ij}(\mathbf{r}_2)\) the pair distribution and \(r_{21} = r_2 - r_1\). Among the most known closures between \(h_{ij}(\mathbf{r}_2)\) and \(c_{ij}(\mathbf{r}_2)\) used to solve Eq. (1), we have \(34\).

\[
c_{ij}(\mathbf{r}_2) = -\beta u_{ij}(\mathbf{r}_2) + h_{ij}(\mathbf{r}_2),
\]

(2)

\[
c_{ij}(\mathbf{r}_2) = f_{ij}(\mathbf{r}_2) \exp\{-\beta u_{ij}(\mathbf{r}_2)\} g_{ij}(\mathbf{r}_2),
\]

(3)

\[
c_{ij}(\mathbf{r}_2) = -\beta u_{ij}(\mathbf{r}_2) \text{ for } r_{21} \equiv |\mathbf{r}_{21}| > a_{ij}.
\]

Eqs. (2) to (4) are known as the hypernetted chain (HNC), the Percus-Yevick (PY) and the mean spherical (MS) approximations, respectively; \(u_{ij}(\mathbf{r}_2)\) is the direct interaction potential between two particles of species \(i\) and \(j\), \(a_{ij}\) is their closest approach distance, \(f_{ij}(\mathbf{r}_2)\) is the excluded volume factor, and \(g_{ij}(\mathbf{r}_2)\) is the pair distribution function.

\[
\exp\{-\beta u_{ij}(\mathbf{r}_2)\} - 1, \text{ and } \beta \equiv 1/k_B T. \text{ Some more possibilities to solve Eq. (1) are originated by considering a closure for } c_{ij}(\mathbf{r}_2) \text{ in the first term of Eq. (1) and a different one for } c_{mij}(\mathbf{r}_{13}) \text{ in the second term of Eq. (1)}, \text{ giving rise to hybrid closures.}
\]

To derive integral equations for inhomogeneous fluids, we let an external field to be one of the fluid species, say \((n+1)\)-species (denoted as the \(\gamma\)-species), which is required to be infinitely dilute, i.e., \(\rho_\gamma \to 0\). Therefore, the total correlation function between a \(\gamma\)-species particle and a \(j\)-species particle is given by

\[
h_{\gamma j}(\mathbf{r}_2) = c_{\gamma j}(\mathbf{r}_2) + \sum_{m=1}^{n} \rho_m \int h_{\gamma m}(\mathbf{r}_{23})c_{mj}(\mathbf{r}_{13}) \, dv_3
\]

with \(j = 1, \ldots, n\).

The total correlation functions for the remaining species satisfy a \(n\)-component Ornstein-Zernike equation as Eq. (1) (with no \(\gamma\) species) from which \(c_{mij}(\mathbf{r}_{13})\) is obtained. In this scheme, the pair correlation functions, \(g_{j\gamma}(\mathbf{r}_2)\), is just the inhomogeneous one-particle distribution function, \(g_{j}(\mathbf{r}_1)\), for particles of species \(j\) under the influence of an external field. Thus, \(h_{\gamma j}(\mathbf{r}_2)\) and \(c_{\gamma j}(\mathbf{r}_2)\) can be replaced with \(h_{j}(\mathbf{r}_1)\) and \(c_{j}(\mathbf{r}_1)\), respectively. Thus, the inhomogeneous local concentration for the \(j\) species is given by

\[
\rho_j(\mathbf{r}_1) = \rho_j g_j(\mathbf{r}_1),
\]

(6)

By using the HNC closure (Eq. (1)) for \(c_{\gamma j}(\mathbf{r}_2)\) in Eq. (1), we get

\[
g_j(\mathbf{r}_1) = \exp\left\{-\beta u_j(\mathbf{r}_1) + \sum_{m=1}^{n} \rho_m \int h_{j m}(\mathbf{r}_{3})c_{mj}(\mathbf{r}_{13}) \, dv_3 \right\},
\]

(7)

where the subindex \(\gamma\) has been omitted for consistency with Eq. (6). In our approach, \(c_{mij}(\mathbf{r}_{13})\) is approximated by the direct correlation function for a \(n\)-component homogeneous fluid. Thus, \(c_{mij}(\mathbf{r}_{13})\) is obtained from Eq. (1) using one of the closures provided by Eqs. (2)–(4). For the present derivation we will use \(c_{mij}(\mathbf{r}_{13})\) obtained with the MS closure (Eq. (4)), therefore, we obtain the hypernetted chain/mean spherical (HNC/MS) integral equations for an inhomogeneous fluid. This equation has shown to be particularly successful in the case of inhomogeneous charged fluids when it is compared with molecular simulation data.

B. The semipermeable membrane and fluid models

The membrane is modelled as a planar hard wall of thickness \(d\), and charge densities \(\sigma_1\) and \(\sigma_2\) on each surface and separates two fluid phases, referred as \(\alpha\) and \(\beta\). In Fig. 1 \(\sigma_1\) and the \(\alpha\)-phase are at the left hand side, whereas \(\sigma_2\) and the \(\beta\)-phase are at the right hand side. The fluid phases are made up in the following way:
The membrane dielectric constant is considered equal to that of the solvent. Furthermore, it is assumed that the membrane is homogeneous and neutral, i.e., the neutrality condition is written as

$$\sum_{i=1}^{2} z_i \rho_i^a = \sum_{i=1}^{3} z_i \rho_i^\beta = 0,$$

with \( m, j = 1, \ldots, 3 \) and \( a_{m,j} = \frac{a_m + a_j}{2} \). Far away from the membrane each phase is homogeneous and neutral, thus the neutrality condition is written as

$$\sum_{i=1}^{2} z_i \rho_i^a = \sum_{i=1}^{3} z_i \rho_i^\beta = 0,$$

being \( \rho_i^a \) and \( \rho_i^\beta \) the bulk concentrations of the \( i \) species in the \( \alpha \) and \( \beta \) phases, respectively. The charge on the membrane is compensated by an excess of charge in the fluid (per unit area), \( \sigma' \):

$$\sigma' \equiv \sigma^\alpha + \sigma^\beta = -\sigma_T,$$

with \( \sigma_T = \sigma_1 + \sigma_2 \) and being \( \sigma^\alpha \) and \( \sigma^\beta \) the excess of charge in the \( \alpha \)-phase and \( \beta \)-phase, respectively, which are given by

$$\sigma^\alpha = \int_{-\frac{d}{2}}^{\frac{d}{2}} \rho_{el}(x) \, dx$$

and

$$\sigma^\beta = \int_{\frac{d}{2}}^{\infty} \rho_{el}(x) \, dx,$$

being

$$\rho_{el}(x) \equiv e \sum_{m=1}^{3} \frac{1}{z_m \sigma_m(x)}.$$

The interaction potential between the membrane and a \( j \)-species particle depends only on the particle position, \( x \), referred to a coordinate system set in the middle of the membrane and measured perpendicularly. Thus, we write \( u_j(x) \) which is split as \( u_j(x) = u_j^d(x) + u_j^e(x) \), being \( u_j^d(x) \) the direct electrostatic potential and \( u_j^e(x) \) the hard-core interaction. The former can be found from Gauss’ law, resulting

$$-\beta u_j^d(x) = \begin{cases} \frac{2\pi}{\varepsilon} z_j e \beta \sigma_T (x - L) & \text{for } x \geq \frac{d}{2}, \\ \frac{2\pi}{\varepsilon} z_j e \beta [\sigma_T (-x - L) - (\sigma_1 - \sigma_2) d] & \text{for } x \leq \frac{d}{2}. \end{cases}$$

where \( L \) is the location of a reference point. The hard-core interaction is given by

$$u_j^e(x) = \begin{cases} \infty & \text{for } |x| < \frac{d + a_j}{2}, \\ 0 & \text{for } |x| \geq \frac{d + a_j}{2}. \end{cases}$$

for \( j = 1, 2 \). For the impermeable species (\( j = 3 \))

$$u_3^e(x) = \begin{cases} \infty & \text{for } x < \frac{d + a_3}{2}, \\ 0 & \text{for } x \geq \frac{d + a_3}{2}. \end{cases}$$
This potential imposes \( g_\alpha(x) = 0 \) for \( x \leq -d/2 \).

In Eq. \( \text{(17)} \) we use the expression of \( c_{mj}(r_{13}) \) for a primitive model bulk electrolyte, which has an analytical expression, written as

\[
c_{mj}(r_{13}) = \begin{cases} 
-\beta u_{mj}^d(r_{13}) &= -\beta z_m z_e e^2 / \varepsilon \quad \text{for } r_{13} \geq a_{mj}, \\
0 &= \text{for } r_{13} < a_{mj}, 
\end{cases}
\]

where \( r_{13} = |r_{13}| \) is the relative distance between two ions of species \( m \) and \( j \). The particles short range correlations are considered through the \( c_{mj}^\alpha(r_{13}) \) and \( c_{mj}^\beta(r_{13}) \). The explicit form of these functions is given in appendix A. The integral in Eq. \( \text{(17)} \) can be expressed in cylindrical coordinates, and analytically calculated in the \( \phi \) and \( r \) variables (see Fig. \( \text{H} \)). Let us consider a cylinder coordinate system where \( r_{13}^2 = x^2 + y^2 + z^2 - 2xy \) and \( dv_3 = drd\phi dy \). After a lengthy algebra, from Eq. \( \text{(17)} \) we get \( \text{(19)} \) for \( j \)

\[
g_j(x) = \exp \left\{ \frac{2\pi}{\varepsilon} z_j e \beta (\sigma_1 + \sigma_2) |x| - 2\pi A_j(x) \right\} + 2\pi \sum_{m=1}^2 \rho_m \int_{-\infty}^{d_{13}^+} h_m(y) G_{mj}(x,y) dy \\
+ 2\pi \sum_{m=1}^3 \rho_m \int_{d_{13}^+}^{\infty} h_m(y) G_{mj}(x,y) dy \\
+ 2\pi \frac{e^2 \beta}{\varepsilon} \sum_{m=1}^2 z_m \rho_m \int_{-\infty}^{d_{13}^+} g_m(y) [y + |x - y|] dy \\
+ 2\pi \frac{e^2 \beta}{\varepsilon} \sum_{m=1}^3 z_m \rho_m \int_{d_{13}^+}^{\infty} h_m(y) [y + |x - y|] dy 
\]

The first and third integrals include \( h_i(y) = g_j(y) - 1 \) for particles in the \( \alpha \)-phase whereas, the second and fourth integrals, for particles in the \( \beta \)-phase. Notice the different summation limits due to the different phase composition. We have defined

\[
G_{mj}(x,y) = L_{mj}(x,y) + K_{mj}(x,y),
\]

\[
L_{mj}(x,y) = \int_{|x-y|}^{\infty} c_{mj}^\alpha(r_{13}) r_{13} dr_{13} = \frac{e^2 \beta}{\varepsilon} D_{mj}(x,y)
\]

\[
K_{mj}(x,y) = \int_{|x-y|}^{\infty} c_{mj}^\beta(r_{13}) r_{13} dr_{13},
\]

and

\[
A_j(x) = \rho_3 \int_{-\infty}^{d_{13}^+} G_{3j}(x,y) dy \\
+ 2\sum_{m=1}^2 \rho_j \int_{-\infty}^{d_{13}^+} G_{mj}(x,y) dy \\
+ z_j z_3 \beta e^2 \int_{-\infty}^{d_{13}^+} [y + |x - y|] dy \\
+ z_j e \frac{\beta d}{\varepsilon} (\sigma_1 - \sigma_2) \Theta(x + d/2),
\]

with \( \Theta(x) \) the step function, defined as

\[
\Theta(x) = \begin{cases} 
0 & \text{for } x < 0, \\
1 & \text{for } x \geq 0.
\end{cases}
\]

The expressions for the kernels, \( K_{mj}(x,y) \) and \( D_{mj}(x,y) \), are given in appendix A.

From the solution of Eq. \( \text{(17)} \) one obtains the reduced concentration profile, \( \rho_j(x) = \rho_j g_j(x) \). The bulk concentrations of species \( j \), at the \( \alpha \) and \( \beta \) phases (\( \rho_j^\alpha \) and \( \rho_j^\beta \)) are given by

\[
\rho_j^\beta = \lim_{x \to \infty} \rho_j g_j(x),
\]

\[
\rho_j^\alpha = \lim_{x \to -\infty} \rho_j g_j(x),
\]

respectively. At the \( \beta \) phase \( g_j(x) \to 1 \) as \( x \to \infty \) then \( \rho_j^\beta = \rho_j \). On the other hand, in the \( \alpha \) phase (for \( x < 0 \), \( \lim_{x \to -\infty} g_j(x) \neq 1 \)). It must be pointed out that the electrolyte bulk concentration at the \( \alpha \)-phase (\( \rho_j^\alpha \), for \( j = 1, 2 \)) satisfy the bulk electroneutrality condition, Eq. \( \text{(10)} \), and are a result from the theory.

C. Computation of the osmotic pressure: contact theorem

Let us consider a slice of fluid of width \( dx \), area of its faces, \( A \), parallel to the membrane and located at \( x \). The force on the slice in the \( x \) direction, \( df_x \), is given by

\[
df_x = E_x(x)dx + Sdp(x)
\]

being \( E_x(x) \) the electric field in the \( x \) direction at \( x \), \( dQ \) the total charge in the fluid slice and \( dp(x) \) the pressure difference at the two faces. Taking into account that

\[
E_x(x) = -\frac{\partial \psi(x)}{\partial x},
\]

and using Poisson’s equation,

\[
\frac{\partial^2 \psi(x)}{\partial x^2} = -\frac{4\pi}{\varepsilon} \rho_{el}(x),
\]

we write

\[
dQ = A\rho_{el}(x)dx = -\frac{A\varepsilon}{4\pi} \left( \frac{\partial^2 \psi(x)}{\partial x^2} \right) dx
\]

Thus, we rewrite Eq. \( \text{(27)} \) as

\[
dF_x(x) = \frac{A\varepsilon}{4\pi} \left( \frac{\partial \psi(x)}{\partial x} \right) \left( \frac{\partial^2 \psi(x)}{\partial x^2} \right) dx + Adp(x)
\]

or equivalently,

\[
dF_x(x) = \frac{A\varepsilon}{8\pi} \frac{\partial}{\partial x} \left( \frac{\partial \psi(x)}{\partial x} \right)^2 dx + Adp(x)
\]
Considering that in equilibrium \(dF_\alpha(x) = 0\) and integrating Eq. (32) in the interval \([d/2, \infty)\) with the boundary condition
\[
\lim_{x \to \infty} \frac{\partial \psi(x)}{\partial x} = 0, 
\]
we obtain
\[
\varepsilon \left( \frac{\partial \psi(x)}{\partial x} \right)^2_{x = d/2} + (p_0^\beta - \Pi^\beta) = 0, 
\]
where \(\Pi^\beta \equiv \lim_{x \to \infty} p(x)\) is the bulk fluid pressure and the expression for the pressure on the membrane right surface, \(p_0^\beta \equiv p(0)\), is given by
\[
p_0^\beta = k_B T \rho_T^\beta(0) = k_B T \sum_{i=1}^{3} \rho_i g_i \left( \frac{d + a_i}{2} \right), 
\]
where \(\rho_T^\beta(0) = \sum_{i=1}^{3} \rho_i \left( (\frac{d}{a} + 1) \right)\). Eq. (35) is an exact relationship which can be obtained by considering the force on the fluid (at the contact plane) exerted by the hard wall. From basic electrostatics we have
\[
\varepsilon \left( \frac{\partial \psi(x)}{\partial x} \right)^2_{x = d/2} = \int_{d/2}^{\infty} \rho_{el}(x) \, dx, 
\]
thus, using Eqs. (34), (35) and (36) we can write
\[
\Pi^\beta = \frac{2\pi}{\varepsilon} \left[ \int_{d/2}^{\infty} \rho_{el}(x) \, dx \right]^2 + k_B T \sum_{i=1}^{3} \rho_i g_i \left( \frac{d + a_i}{2} \right), 
\]
where the first term can be identified as the Maxwell stress tensor. A similar expression is obtained for the bulk pressure in the \(\alpha\) phase
\[
\Pi^\alpha = \frac{2\pi}{\varepsilon} \left[ \int_{-\infty}^{-d/2} \rho_{el}(x) \, dx \right]^2 + k_B T \sum_{i=1}^{2} \rho_i g_i \left( \frac{-d + a_i}{2} \right). 
\]
The osmotic pressure, \(\Pi\), is defined as
\[
\Pi = \Pi^\beta - \Pi^\alpha. 
\]
From of Eqs. (12), (37) and (38), Eq. (39) becomes,
\[
\Pi = \frac{2\pi}{\varepsilon} \left\{ [\sigma^\beta]^2 - [\sigma^\alpha]^2 \right\} + k_B T \sum_{i=1}^{3} \rho_i g_i \left( \frac{d + a_i}{2} \right) 

- k_B T \sum_{i=1}^{2} \rho_i g_i \left( \frac{-d + a_i}{2} \right). 
\]

Due to the fluid-fluid correlation across a thin membrane, the induced charge densities (\(\sigma^\alpha\) and \(\sigma^\beta\)) and \(g_i (\pm \frac{d + a_i}{2})\) depend on the fluid conditions \((\rho_i, z_i, a_i, \text{ with } i = 1, 2, 3)\) and on the membrane parameters \((\sigma_1, \sigma_2 \text{ and } d)\). The computed value of \(\Pi\) (using \(\sigma^\alpha\), \(\sigma^\beta\) and \(g_i (\pm \frac{d + a_i}{2})\)) from HNC/MS, however, does not depend on the membrane parameters. We have numerically corroborated this fact by computing \(\Pi\) for several values of \(\sigma_1, \sigma_2 \text{ and } d\). This is physically appealing since the pressure can only depend on the bulk fluid conditions at both sides of the membrane. However, we had to do very precise calculations of \(g_i(x)\), particularly in the neighborhood of \(x = \pm \frac{d + a_i}{2}\), to prove the above statement.

Eq. (40) is an exact theorem to compute the osmotic pressure, \(\Pi\), in terms of microscopic quantities. A similar expression for the osmotic pressure was derived by Zhou and Stell [25]. However, the differences between the current derivation and that of those authors are due to the ions-membrane short range interactions. If we use, in the Zhou and Stell theory, the hard wall interaction between the permeable ions and the membrane (provided by Eq. (14)), we recover Eq. (40).

III. RESULTS AND DISCUSSION

Several physical effects determine particles adsorption on the charged membrane. One of the most relevant is the membrane-particle direct interaction energy, which, at the surface is given by
\[
U_i = q_i u_i \left( \frac{a_i}{2} \right) = \frac{2\pi q_i \sigma}{\varepsilon} \left( L - \frac{a_i}{2} \right), 
\]
being \(L\) the location of a reference point. The more negative the value of \(U_i < 0\), particles adsorption is energetically more favorable. Many body correlations play also an important role in the adsorption phenomena and are responsible for the surface-particle forces of non-electrostatic origin. Although it is not possible to sharply

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**FIG. 2**: Reduced concentration profiles (RCPs) for a macroions solution \((\rho_M = 0.01\text{M}, z_M = -10)\) in a monovalent electrolyte \((\rho_+ = 1.1\text{M} \text{ and } \rho_- = 1.0\text{M})\), with \(a_3 = 3.8a\), \(\sigma_1 = \sigma_2 = 0.272 C/m^2\text{a}\) and \(d = a\). The continuous, dashed and dotted lines represent the RCPs for the macroions, anions and cations, respectively.
For our discussion it is useful to follow the following concepts: When the amount of adsorbed charge exceeds what is required to screen the surface charge, it is said to occur a surface charge reversal (CR). In consequence, at certain distance from the surface the electric field is inverted. Next to the CR layer, a second layer of ions (with same charge sign as that of the surface) is formed, producing a charge inversion (CI) of the electrical double layer \([37, 50]\). Such a denomination (charge inversion) is originated from the fact that ions invert their role in the diffuse layer. In the past, we have shown that charge reversal and charge inversion are many body effects and are induced by a compromise between short range correlations \((\xi_T)\) and electrostatic long range correlations \((\xi_{ij})\) \([37, 51]\).

The HNC/MS equations for a semipermeable membrane, Eqs. \([10, 13]\), are numerically solved using a finite element technique \([51, 52]\). From the solution of HNC/MS equations the reduced concentration profiles (RCPs), \(g_j(x)\), are obtained. In the discussion, we adopted the following notation: \(z_1 = z_+\), \(z_2 = z_-\) and \(z_3 = z_M\) for the number valence of cations, anions and macroions, respectively; idem for \(\rho_1\) and \(\alpha_i\). In all our calculations we have used fixed values of \(T = 298K\), \(\varepsilon = 78.5\) and \(a = 4.25\) Å. The effects of salt valence, macroions size, and membrane surface charge density on macroions adsorption are analyzed. Thus, we consider macroions \((\rho_M = 0.01M\) and \(z_M = 10\)) in a monovalent electrolyte \((\rho_+ = 1.1M\) and \(\rho_- = 1.0M\)) and (b) divalent \((\rho_+ = 0.55M\) and \(\rho_- = 0.5M\)) electrolyte solutions. For each case, we considered two macroion sizes \((\alpha_M = 3.8a\) and \(\alpha_M = 7a\)) and three values for the membrane charge densities: i) \(\sigma_1 = \sigma_2 = 0.272C/m^2\), ii) \(\sigma_1 = \sigma_2 = -0.272C/m^2\) and iii) \(\sigma_1 = 0.68C/m^2, \sigma_2 = -0.136C/m^2\). Finally, we show calculations for the osmotic pressure (as a function of the macroion concentration) compared with experimental results.

### A. Macroions in a monovalent electrolyte \((z = 1)\)

In this subsection we discuss the case of macroions \((z_M = 10)\) in a monovalent electrolyte solution \((\rho_+ = 1.1M, \rho_- = 1.0M, z_+ = z_- = 1)\).

#### 1. Positively charged membrane

In Fig. 2 we present the RCPs when the membrane is positive and symmetrically charged \((\sigma_1 = \sigma_2 = 0.272C/m^2)\), the membrane thickness is \(d = a\) and \(\alpha_M = 3.8a\). As a result, we obtained the asymptotic values of the distribution functions in the \(\alpha\)-phase, \(g_-(\infty) = 1.0758\) and \(g_+(\infty) = 0.9779\), such that Eq. \([10]\) is satisfied. In both phases we observe that the negative ions are adsorbed and the positive ions expelled, as it is expected. In the \(\beta\)-phase we observe that the adsorption of macroions is more favorable than the
adsorption of negative small ions. This is understood in
terms of the electrostatic energy of one particle of species
\(i\) at the membrane surface, \(U_i\): since \(|z_M| > |z_-|\), from
Eq. (41) it is easy to see that \(U_M < U_- < 0\), which favors
macroions adsorption. As we pointed out above, many
body correlations also influence adsorption. In this case
macroion-macroion long range correlations are predomin-
antly more important than the ion-ion correlations since
\(\xi_M \approx 7\xi_-\). Short range correlations are also important
and play an important role in the macroions adsorption:
an increment of macroions concentration (keeping con-
stant \(a_M\) and \(z_M\)) implies an increment of \(\eta_T\) and pro-
duces an increment of the macroions adsorption. How-
ever an increment of \(\eta_T\) not always is followed by an
increase of the adsorption as it will be noticed in the
discussion of Fig. 3. In the macroions RCP we find a
first macroions layer next to the membrane surface, af-
ter this layer there is a region where the macroions are
completely expelled and then a small second peak. The
negative small ions are also adsorbed to the membrane’s
surface but their concentration is smaller than for the
macroions. The RCP for positive ions show that these
are completely expelled from the membrane right surface.
However, a peak in the RCP is found at \(x \approx 4.3a\) which
is the ion-surface distance when there is a macroion in
between. This peak implies an effective surface-cation
attraction due to a field inversion caused by the surface
CR.

Fig. 3 shows the results obtained for the same sys-
tem as in Fig. 2 except that the macroions are larger,
\(a_M = 7a\). At the \(\alpha\)-phase the distribution function have
the same qualitative behavior as in Fig. 2 however, in
this case \(g_-(\infty) = 1.1938\) and \(g_+(\infty) = 1.0853\), i.
.e., the amount of salt in the \(\alpha\)-phase increases by in-
creasing the macroions size. Respect to Fig. 2 a decre-
ment of macroions adsorption is observed in Fig. 3. The
increment of the macroions diameter implies a decre-
ment of the macroions-macroions long range correlations
(in this case \(\xi_M \approx 2\xi_-\)) and an increment of \(\eta_T\), and
hence, an increment of the contributions arising from
correlations of short range nature. Such an increment,
however, does not increase (but decrease) the macroions
adsorption. This is understood in terms of Eq. (41)
\([U_M(a_M = 3.8a) < U_M(a_M = 7a)]\) which implies that
the adsorption is energetically less favorable for \(a_M = 7\)
than for smaller macroions with the same charge.

2. Negatively charged membrane

Fig. 4 shows the RCPs when the membrane is negative
and symmetrically charged (\(\sigma_1 = \sigma_2 = -0.272C/m^2\))
for \(a_M = 3.8a\). The membrane thickness is \(d = a\).
The asymptotic value of the distributions function does
not depend on the membrane’s charge and thickness,
hence, the \(g_i(\infty)\) have the same value as in Fig. 2.
The RCP for small ions behave in a normal way in the
sense that positive ions are attracted to the to the mem-
brane surface, whereas the negative ions are expelled
from it. In the \(\beta\)-phase, it is observed that macroions
are expelled from the membrane surface for \(x < 6a/2\).
After this zero concentration region, an small peak in
the macroions RCP is observed at \(x \approx 9a/2\) indicat-
ing an effective macroion-membrane attractive force and
an slight surface CR produced by the small cations. At
these electrolyte conditions (1 : 1 and \(\rho_+ = 1M\) with
no macroions), cations display a monotonically decaying
distribution profile [12], hence, the oscillatory behavior
of the RCPs for the small ions (in the \(\beta\)-phase) is a con-
sequence of the presence of macroions. By considering
the macroions size \(a_M = 7.0\) (not shown), the qualita-
tive behavior of the RCPs is similar to that of Fig. 3
with the following differences: (i) the RCPs oscillations
of the small ions at the \(\beta\)-phase are of longer range and
(ii) the macroions RCP maximum is higher. This fact
points out the relevance of the effect of the particles size
and concentration (particles volume fraction) in the effec-
tive attraction between like charged particles in solution
\(30, 31, 32, 33, 34\).

From the analysis presented from Fig. 2 to 4 we see
that macroions adsorption increases by increasing \(\eta_T\), \(\xi_M\)
and \(-U_M\). However, we point out the following findings:
when macroions and the surface are oppositely charged,
long range electrostatic correlations dominate over short
range correlations. Hence, adsorption is enhanced by in-
creasing \(\xi_M\) and/or \(-U_M\). On the other hand, when
macroions and the surface are like charged the mecha-
nism for macroions adsorption (mediated by the small
ions) is mainly driven by short range correlations, thus,
adsorption increases by increasing \(\eta_T\) even though \(\xi_M\)
decreases.
In both cases the results are qualitatively similar.

For a sufficiently large membrane’s thickness the induced charge in each fluid phase screens its corresponding membrane surface, i.e., \( \sigma_\alpha \to -\sigma_1 \) and \( \sigma_\beta \to -\sigma_2 \) as \( d \to \infty \). At \( d = 100a \) each fluid has screened its respective surface charge density. Here we show a comparison between the results obtained for \( a_M = 3.8a \) and \( a_M = 7a \). In both cases the results are qualitatively similar.

3. Unsymmetrically charged membrane

In Fig. 6 it is shown the RCPs at the two membrane sides for a macroions diameter \( a_3 = 3.8a \) and \( d = a \). The membrane is unsymmetrically charged with \( \sigma_1 = 0.68 \) C/m\(^2\) and \( \sigma_2 = -0.136 \) C/m\(^2\). At the right hand side surface macroions and small anions (negatively charged) are adsorbed on the membrane, in spite of \( \sigma_2 < 0 \). The adsorption of negatively charged particles on a negatively charged surface is due to the correlation between the two fluids. This is understood by considering the following two facts: (i) the membrane has a positive net charge (\( \sigma_T > 0 \)) and (ii) the charge on the left hand side surface (\( \sigma_1 \)) is not completely screened by the excess of charge in its corresponding fluid phase (\( \sigma^\alpha \)), therefore, the electric field produced by \( \sigma_1 + \sigma^\alpha \) overcomes the field produced by \( \sigma_2 \), inducing macroions and anions adsorption. From here, we observed that \( \sigma^\alpha \) and \( \sigma^\beta \) depend on \( d \) as it is discussed below.

In Fig. 6 it is shown the excess of charge densities \( \sigma_\alpha \) and \( \sigma_\beta \), as a function of the membrane’s thickness \( d \). The dependence on the wall thickness of the induced charge densities \( \sigma_\alpha \) and \( \sigma_\beta \), is a manifestation of the correlation between the fluids. The correlation between the two fluids is due to the electrostatic interaction among the particles at both phases but, more importantly, to the fact that they are at constant chemical potential. For a sufficiently large membrane’s thickness the induced charge density in each fluid phase screens its corresponding membrane surface, i.e., \( \sigma^\alpha \to -\sigma_1 \) and \( \sigma^\beta \to -\sigma_2 \) as \( d \to \infty \). At \( d = 100a \) each fluid has screened its respective surface charge density. Here we show a comparison between the results obtained for \( a_M = 3.8a \) and \( a_M = 7a \). In both cases the results are qualitatively similar.

B. Macroions in a divalent electrolyte (\( z = 2 \))

We now discuss the case of macroions (\( z_M = -2 \)) in a divalent electrolyte solution (\( \rho_+ = 0.55M \), \( \rho_- = 0.5M \), \( z_+ = -z = 2 \)).

1. Positively charged membrane

In Fig. 7 we show the RCPs for \( \sigma_1 = \sigma_2 = 0.272 \) C/m\(^2\), \( d = a \) and \( a_M = 3.8a \). At the \( \alpha \)-phase we observe oscillations of the RCPs, which is a typical behavior of a divalent electrolyte. Although we observe a strong adsorption of macroions in the \( \beta \)-phase, the amount of adsorbed small negative ions is even larger (the concentrations of macroions and small negative ions at the interface are \( \rho_M \left( \frac{d+2a}{2} \right) \approx 7.2M \) and \( \rho_- \left( \frac{d+a}{2} \right) \approx 16M \), respectively). Energetically, macroions adsorption should be more favorable, however, macroions adsorption is inhibited because divalent positive ions more efficiently screen macroion-membrane and macroion-macroion interactions. We infer this from the RCP for cations, which displays two small peaks at \( x \approx 2a \) and \( x \approx 4.3a \). The first peak corresponds to a positive ions layer contiguous to the negative ions adsorbed on the wall. The position of the second peak corresponds to a positive ions layer next to the macroions layer. This structure indicates that positive ions surround macroions due to their strong electrostatic interaction, in this case \( \xi_{M+} \approx -8.3 \frac{ek_BT_0}{e^2} \approx -14 \), whereas for macroions in a monovalent electrolyte \( \xi_{M+} \approx -7 \). By comparison of Figs. 6 and 7 we see that macroions (next to an oppositely charged surface) are
better adsorbed when they are in a monovalent solution rather than in a multivalent solution: for this particular case of macroions ($\rho_M = 0.01 M, z_M = -10$ and $a_M = 3.8a$), $\rho_M(M_{\alpha + 
abla}) = 20M$ when macroions are in a monovalent electrolyte, whereas $\rho_M(M_{\alpha + 
abla}) \approx 7.2M$ when macroions are in a divalent electrolyte.

In Fig. 8 we show the RCPs for the same conditions as in Fig. 7 but with $a_M = 7a$. Although macroions adsorb in the $\beta$-phase, they do not influence significantly on the local concentration of small ions. Hence, we see that the RCPs for small ions are quantitatively similar in both phases: the concentrations of counterions at the membrane surfaces are $\rho(\pm \frac{d+\nabla}{2}) \approx 22.5M$, in addition, the RCPs maxima are located symmetrically around $x \approx \pm 1.7a$. The adsorption of macroions decrease (respect to Fig. 7) due to the efficient screening of the membrane charge by the small negative ions and because the adsorption of larger ions (keeping $z_M$ constant) is energetically less favorable, as it was pointed out in the discussion of Fig. 8. We see that the layer of cations around macroions (seen in Fig. 8) disappears due to the decrement of their coulombic interaction, in this case $\xi_{M+} \approx -7.6$.

2. Negatively charged membrane

In Fig. 9 we show the RCPs for a negatively charged macroions solution ($\rho_M = 0.01M, z_M = -10$) in a divalent electrolyte ($\rho_+ = 0.55M$ and $\rho_- = 0.5M$), with $a_M = 3.8a$, $\sigma_1 = \sigma_2 = -0.272 C/m^2$ and $d = a$. The lines meaning is the same as in Fig. 7.

In Fig. 10 we show the RCPs at the two phase for $\sigma_1 = 0.68C/m^2, \sigma_2 = -0.136C/m^2, a_M = 3.8a$ and $d = a$. The correlation between the two fluids is manifested by the attraction of negatively charged particles towards the negatively charged surface at the $\alpha$-phase. However, the adsorption of macroions is quite less efficient than in the monovalent electrolyte case of Fig. 9. In the monovalent case the contact value of the local concentration is $\rho_M(M_{\alpha + \nabla}) \approx 2.7M$ whereas in this case it is $\rho_M(M_{\alpha + \nabla}) \approx 0.12M$. This is due mainly to the more efficient field screening by the divalent electrolyte at the left hand side surface. In the monovalent ele-
trolute case the induced charge density at the $\alpha$-phase is $\sigma_\alpha = -0.43 \text{C/m}^2$ when $d = a$ whereas in the divalent electrolyte case $\sigma_\alpha = -0.50 \text{C/m}^2$.

### C. The osmotic pressure

Although the adsorption of macroions is strongly influenced by the membrane surface charge and thickness, we observe however, that the osmotic pressure does not depend on these membrane properties as it has been pointed out in subsection II C. In Fig. 11 we show the osmotic pressure (obtained from HNC/MS theory) as a function of the macroions concentration $\rho_M$, for two macroion sizes. This plot shows the osmotic pressure for macroions in a monovalent electrolyte and in a divalent electrolyte. The osmotic pressure increases by increasing the particles excluded volume (either $\rho_M$ or $a_M$), on the other hand, it is not observed a qualitative difference between the curves for the osmotic pressure of macroions in a monovalent and divalent electrolytes.

Computation of the osmotic pressure of proteins solutions is an issue addressed by some authors. Results of particular interest are those for albumin solutions, for which theoretical calculations and measurements of the osmotic pressure have been reported. In Fig. 11 we show the osmotic pressure predictions of HNC/MS theory (as a function of the protein concentration) and experimental results. The experimental data correspond to a solution of albumin in a 0.15M NaCl aqueous solution. In accordance with titration measurements, the albumin has a net charge of $Q = -9e$ and $Q = -20e$ for pH$= 5.4$ and pH$= 7.4$, respectively, in our calculations we have used $a_M = 62\text{Å}$ which corresponds to the experimental protein diameter. It is remarkable the excellent agreement between theory and experiment as well as the fact that no adjustable parameters have been used. The prediction of HNC/MS fits well the experimental data even for protein concentration as high as 30% the protein volume in solution (which is estimated assuming the albumin molecular weight $w_{al} = 69\text{Kg/mol}$). For higher protein concentration, HNC/MS shows discrepancies with experimental measurements which may be associated with the following facts: (i) the albumin molecule is not spherically symmetric as in the model, therefore, the protein geometry becomes relevant when the protein volume fraction is high, (ii) integral equations are approximated theories, meaning that they do not take into account all the particle correlations.

### IV. CONCLUSIONS

We studied a model charged membrane separating two fluid phases ($\alpha$ and $\beta$). The $\beta$-phase phase contains macroions in an electrolyte solution and the $\alpha$-phase is a simple electrolyte solution. The system is modeled in such a way that the small ions at both phases are at the same chemical potential, thus, the membrane is considered to be semipermeable. It is important to point out that we considered explicitly the effect of particles size (short range correlations) and electrostatic long range correlations. Here we have applied the hypernetted chain/mean spherical integral equations to the semipermeable membrane model. Also we have derived the equation for the osmotic pressure through a simple forces bal-
The curves are obtained from Eq. (12) using a \( M_w = 62 \pm 54 \), \( \sigma = 4.25 \pm 54 \) and \( \varepsilon = 1.0 \pm 54 \).

By solving the HNC/MS integral equations we obtained the particles concentration profiles which allowed us to study the adsorption of macroions on the membrane. We analyzed the influence of several factors in the macroions adsorption: membrane surface charge, membrane thickness, the effect of salt and macroions size. From this study we emphasize the following results: 1) When the membrane and macroions are oppositely charged the adsorption is energetically favorable, however, if multivalent ions are present the membrane-macroions interaction is screened which is unfavorable for macroions adsorption. On the other hand, the larger the macroions (keeping the same charge and concentration) the adsorption is energetically less favorable. 2) The attraction of macroions towards a like-charged surface seems to be energetically unfavorable. Nevertheless, in our model, we find that such an attraction is feasible and it is due to short range correlations, which are properly considered in our theory. These previous results are not a consequence of the permeability condition but are general. 3) As a consequence of the permeability condition constant chemical potential, we have that for an unsymmetrically charged membrane the fluids correlation may produce adsorption of charged macroions on a like charged surface. In addition, the permeability condition implies a non trivial relation between the induced charge densities (\( \sigma^\alpha \) and \( \sigma^\beta \)) and the membrane thickness. The theory predictions are robust as it is shown by the excellent agreement between theory and experiment where we have not used adjustable parameters. The results of this work could be technologically relevant for the design of selective membranes.

V. ACKNOWLEDGMENTS

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APPENDIX A: APPENDIX

1. The Mean Spherical Closure

The primitive model is the simplest model for an electrolyte that includes many relevant aspects of real solutions. In the general case the primitive model is constituted by \( n \)-species of particles, with the mixture is embedded in a uniform medium of dielectric constant \( \varepsilon \) at temperature \( T \). Each species is defined by the particles point charge at the center, \( q_i = z_i e \) (where \( e \) stands for the proton’s charge and \( z_i \) for the ionic valence), the ionic diameter, \( a_i \), and number concentration, \( \rho_i \). The fluid is constrained to the following condition

\[
\sum_{i=1}^{n} z_i \rho_i = 0. \tag{A1}
\]

The expressions for the direct correlation functions, \( c_{ij}(r_{13}) \), for a bulk electrolyte (required in Eq. (7)) were obtained by Blum and Hiroike through the MS closure, and are written as

\[
c_{ij}(r_{13}) = \frac{e^2 \beta}{\varepsilon} d_{ij}(r_{13}) + c_{ij}^{hs}(r_{13}) - \beta \frac{z_i z_j e^2}{\varepsilon r_{13}}. \tag{A2}
\]

with \( c_{ij}^{ef}(r_{13}) = \frac{e^2 \beta}{\varepsilon} d_{ij}(r_{13}) \), \( \beta = 1/k_B T \) and

\[
d_{ij}(r_{13}) = \begin{cases} b_{ij}^{(1)} + \frac{z_i z_j}{r_{13}} & \text{for } 0 \leq r_{13} \leq \lambda_{ij}, \\ b_{ij}^{(2)} + \frac{z_i z_j}{r_{13}} - b_{ij}^{(3)} r_{13} + b_{ij}^{(4)} r_{13} + b_{ij}^{(5)} r_{13}^3 & \text{for } \lambda_{ij} < r_{13} \leq a_{ij}, \\ 0 & \text{for } r_{13} > a_{ij}. \end{cases} \tag{A3}
\]

with \( \lambda_{ij} = \frac{|a_i - a_j|}{2} \) and \( a_{ij} = \frac{a_i + a_j}{2} \). The constants

\[
D_{a,\lambda} = \frac{0.15 M \text{NaCl at pH}=7.4}{e}
\]

\[
\lambda_{ij} = \frac{|a_i - a_j|}{2}
\]

\[
a_{ij} = \frac{a_i + a_j}{2}
\]
in Eq. (A3) are given by

\[
\begin{align*}
s_i &= (n_i + \Gamma x_i), \\
b_{ij}^{(1)} &= 2[z_i n_j - x_i s_i + \frac{a_i}{3} s_j^2], \\
b_{ij}^{(2)} &= (a_i - a_j) \left\{ \frac{(x_i + x_j)}{4} [s_i - s_j] - \frac{(a_i - a_j)}{16} [(n_i + \Gamma x_i + n_j + \Gamma x_j)^2 - 4n_i n_j] \right\}, \\
b_{ij}^{(3)} &= (x_i - x_j) (n_i - n_j) + (x_i^2 + x_j^2) \Gamma + (a_i - a_j) n_i n_j - \frac{1}{3} [a_i s_i^2 + a_j s_j^2], \\
b_{ij}^{(4)} &= \frac{x_i}{a_i} s_i + \frac{x_j}{a_j} s_j + n_i n_j - \frac{1}{2} [s_i^2 + s_j^2], \\
b_{ij}^{(5)} &= \frac{s_j}{6 a_j} + \frac{s_i}{6 a_i}^2,
\end{align*}
\]

where \( x_i \) are defined as \( x_i = z_i + n_i a_i \) and \( \Gamma \) is obtained from the solution of the following algebraic equation

\[
\Gamma^2 = \frac{\pi c^2}{\varepsilon} \sum_{i=1}^{n} \rho_i (z_i + n_i a_i)^2. \tag{A4}
\]

The \( n_i \) are obtained from the solution of the following set of algebraic equations

\[
-(z_i + n_i a_i) \Gamma = n_i + c a_i \sum_{j=1}^{n} (z_i + n_j a_i), \tag{A5}
\]

where \( c = \frac{\pi}{2} [1 - \frac{\pi}{6} \sum_{i=1}^{n} \rho_i a_i^2]^{-1} \).

Considering that \( a = a_1 = a_2 \), \( c_{ij}^{hs}(r_{13}) \) is just the direct correlation function for a hard spheres \textit{binary} mixture in the PY approximation. For particles of the same size it is given by

\[
c_{ii}^{hs}(r_{13}) = \left\{ \begin{array}{ll}
-A_i - B_i r_{13} - \delta r_{13}^3 & \text{for } r_{13} < a_i, \\
0 & \text{for } r_{13} > a_i.
\end{array} \right. \tag{A6}
\]

For particles of different size we have

\[
c_{ij}^{hs}(r_{13}) = \left\{ \begin{array}{ll}
-A_i - A_j - [\alpha x^2 + 4 \lambda_{13} \delta x^3 + \delta x^4] & \text{for } x \leq \lambda_{13}, \\
-A_i - \frac{[\alpha x^2 + 4 \lambda_{13} \delta x^3 + \delta x^4]}{r_{13}} & \text{for } \lambda_{13} < r_{13} \leq a_{13}, \\
0 & \text{for } r_{13} > a_{13},
\end{array} \right. \tag{A7}
\]

with \( x \equiv r_{13} - \lambda_{13} \). The constants used in Eqs. (A6) and (A7) are given by

\[
A_1 = (1 - \eta_T)^{-3} \left\{ 1 + \eta_T + \eta_T^2 + \frac{\pi}{6} a^3 \rho_T [1 + 2 \eta_T] \right\},
\]

\[
-\frac{\pi}{2} \rho_3 (a_3 - a)^2 \{ a(1 + \eta_3) + a [1 + 2(\eta_1 + \eta_2)] \} \\
+ \frac{\pi a^3}{2} (1 - \eta_T)^{-4} \left\{ \rho_T [1 + \eta_T + \eta_T^2] \right\}, \tag{A8}
\]

\[
B_1 = B_2 = -\pi \left\{ (\rho_1 + \rho_2) a^2 g^{11}_1(a) + \rho_3 a g^{22}_1(a) \right\} (1 - \eta_T)^{-2},
\]

\[
g_{11}(a) = g_{22}(a) = \left\{ \left[ 1 + \frac{1}{2} \eta_T \right] + \frac{3}{2} \eta_T a^3 (a - a_3) \right\} (1 - \eta_T)^{-2},
\]

\[
g_{13}(a) = \frac{[a_3 g_{11}(a) + ag_{22}(a)]}{2a_{13}}. \tag{A12}
\]

The expressions for \( A_3, B_3 \) and \( g_{33}(a_3) \) are obtained by interchanging \( \eta_1 + \eta_2, \rho_1 + \rho_2 \) and \( a_1 \) with \( \eta_1, \rho_1 \) and \( a_3 \), respectively, in the expressions for \( A_1, B_1, g_{11}(a) \).

2. The kernels expressions

Carrying out the integrations indicated in Eqs. (21) and (22), using Eqs. (A3), (A6) and (A7), the expressions for \( K_{ij}(x, y) \) and \( D_{ij}(x, y) \) are

\[
D_{ij}(x, y) = \left\{ \begin{array}{ll}
b_{ij}^{(1)} k_0 + z_i z_j J_1 + b_{ij}^{(2)} M_1 - b_{ij}^{(3)} M_2 + b_{ij}^{(4)} M_3 + b_{ij}^{(5)} M_5, & \text{for } 0 \leq |x - y| \leq \lambda_{ij}, \\
b_{ij}^{(2)} + z_i z_j J_1 - b_{ij}^{(3)} J_2 + b_{ij}^{(4)} J_3 + b_{ij}^{(5)} J_5, & \text{for } \lambda_{ij} < |x - y| \leq a_{ij}, \\
0, & \text{for } a_{ij} < |x - y| \leq a_{ij}.
\end{array} \right. \tag{A13}
\]

\[
-K_{ii}(x, y) = \left\{ \begin{array}{ll}
A_i J_2 + B_i J_3 + \delta J_5, & \text{for } a_{ii} \geq |x - y|, \\
0, & \text{for } a_{ii} < |x - y|. \tag{A14}
\end{array} \right.
\]

\[
-K_{13}(x, y) = \left\{ \begin{array}{ll}
A_1 J_2 + a_0 a_3^3/3 + \delta \lambda_{13} a_4^4 + \delta a_5^5/5, & \text{for } |x - y| < \lambda_{13}, \\
A_1 J_2 + v P_3 + 4 \delta \lambda_{13} P_4 + \delta P_5, & \text{for } \lambda_{13} < |x - y| \leq a_{13}, \\
0, & \text{for } a_{13} < |x - y|. \tag{A15}
\end{array} \right.
\]

where we use the following definitions:

\[
J_n = (a_{ij}^n - |x - y|^{n})/n, \tag{A16}
\]

\[
P_n = (a^n - (|x - y| - \lambda_{ij})^n)/n, \tag{A17}
\]

\[
M_n = (a_{ij}^n - \lambda_{ij}^n)/n, \tag{A18}
\]
and
\[ k_0 = \frac{\lambda^2_{ij} - (x - y)^2}{2}. \]  

\textbf{References:}

[1] Hoppe, W. *Biophysics*; Springer Verlag, Berlin, 1983.
[2] Hiemenz, P. C. *Principles of Colloids and Surface Chemistry*; Marcel Dekker, Inc., New York, 1977.
[3] Tanford, C. *Physical Chemistry of Macromolecules*; John Wiley and Sons, Inc., New York, 1961.
[4] Donnan, F. G. Z. *Elektrochem.* 1911, 17, 572.
[5] Guggenheim, E. A. *Thermodynamics: An Advanced Treatment for Chemists and Physicists*; North Holland Physics Publishing, Amsterdam, 1967.
[6] Vilkov, V. L.; Colton, C. K.; Smith, K. A. *J. of Coll. Int. Sci.* 1980, 79, 548.
[7] Yousef, M. A.; Datta, R.; Rodgers, V. G. J. *J. of Coll. Int. Sci.* 1998, 207, 273.
[8] Gouy, G. *J. Phys.* 1910, 9, 457.
[9] Chapman, D. L. *Philos. Mag.* 1913, 25, 475.
[10] Cuviller, N.; Rondelez, F. *Thin Solid Films* 1998, 327-329, 19.
[11] Torrie, G. M.; Valleau, J. P. *J. Chem. Phys.* 1980, 73, 5807.
[12] Lozada-Cassou, M.; Saavedra-Barrera, R.; Henderson, D. *J. Chem. Phys.* 1982, 77, 5150.
[13] Svensson, B.; Woodward, B. J. C. E. *J. Phys. Chem.* 1990, 94, 2105.
[14] Percus, J. K. in *The Equilibrium Theory of Classical Fluids*; edited by H. L. Frisch and J. L. Lebowitz; W. A. Benjamin, New York, 1964, Chap. II, p. 33.
[15] Evans, R. in *Fundamentals of Inhomogeneous Fluids*; edited by D. Henderson; Marcel Dekker, New York, 1993, Chap. 8.
[16] Zhang, M. Q.; Percus, J. K. *J. Chem. Phys.* 1990, 92, 6799.
[17] Henderson, D.; Abraham, F. F.; Barker, J. A. *Mol. Phys.* 1976, 31, 1291.
[18] Lozada-Cassou, M. J. *Chem. Phys.* 1981, 75, 1412.
[19] Plishchke, M.; Henderson, D. *Electrochim. Acta* 1981, 34, 1865.
[20] Greberg, H.; Kjellander, R. *Mol. Phys.* 1994, 83, 789.
[21] Attard, P. *Adv. Chem. Phys.* 1996, 92, 1.
[22] Decher, G. *Science* 1997, 277, 1232.
[23] Toliver, V.; Smay, J. E.; Braun, P. V.; Lewis, J. A. *PNAS* 2001, 98, 8950.
[24] Zhou, Y.; Stell, G. J. *Chem. Phys.* 1988, 89, 7010.
[25] Zhou, Y. *J. Chem. Phys.* 1988, 89, 7020.
[26] The cavity is immersed in a two component electrolyte plus one macroion species, where the macroions are restricted to be outside the cavity whereas the electrolyte can permeate it.
[27] Lozada-Cassou M.; Yu, J.; *Phys. Rev. Lett.* 1996, 77, 4019.
[28] Lozada-Cassou M.; Yu, J.; *Phys. Rev. E* 1997, 56, 2958.
[29] Aguiular, G. E.; Lozada-Cassou, M.; Yu, J. *J. Coll. Int. Sci.* 2002, 254, 141.
[30] Muthukumar, M. *J. Chem. Phys.* 1996, 105, 5183.
[31] Crocker, J. C.; Matteo, J. A.; Dinsmore, A. D.; Yodh, A. G. *Phys. Rev. Lett.* 1999, 82, 4352.
[32] Kepler, G. M.; Fraden, S. *Phys. Rev. Lett.* 1994, 73, 356.
[33] Crocker, J. C.; Grier, D. G. *Phys. Rev. Lett.* 1996, 77, 1897.
[34] Han Y.; Grier, D. G. *Phys. Rev. Lett.* 2003, 91, 038302.
[35] Bolhuis, P. G.; Louis, A. A.; Hansen, J. P. *Phys. Rev. Lett.* 2002, 89, 128302.
[36] Trokhymchuk, A.; Henderson, D.; Nikolov, A.; Wasan, D. T.; *Phys. Rev. E* 2001, 64, 012401.
[37] Jiménez-Ángeles F.; Lozada-Cassou, M. paper in preparation (see [cond-mat/0309446](http://www.arxiv.org) at [http://www.arxiv.org](http://www.arxiv.org)).
[38] Lozada-Cassou, M. in *Fundamentals of Inhomogeneous Fluids*; edited by D. Henderson; Marcel Dekker, New York, 1993, Chap. 8.
[39] Hansen J. P.; McDonald, I. R. *Theory of Simple Liquids*; Academic Press, London, 2nd ed., 1986.
[40] Degrèe, L.; Lozada-Cassou, M.; Sánchez, E.; González-Tovar, E. *J. Chem. Phys.* 1993, 98, 8905.
[41] Lozada-Cassou, M.; Oliwares, W.; Sulbarán, B.; *Phys. Rev. E* 1996, 53, 522.
[42] Degrèe L.; Lozada-Cassou, M.; *Phys. Rev. E* 1998, 57, 2978.
[43] Deserno, M.; Jiménez-Ángeles, F.; Holm, C.; Lozada-Cassou, M. *J. Chem. Phys.* 2001, 105, 10983.
[44] Lozada-Cassou, M. *J. Chem. Phys.* 1984, 80, 3344.
[45] Lozada-Cassou M.; Díaz-Herrera, E. *J. Chem. Phys.* 1990, 92, 1194.
[46] Oliwares W.; McQuarrie, D. A. *J. Phys. Chem.* 1980, 84, 863.
[47] Carne S. L.; Chan, D. Y. C. *J. Chem. Phys.* 1981, 74, 1293.
[48] Attard, P. *J. Phys. Chem.* 1995, 99, 14174.
[49] Greberg H.; Kjellander, R. *J. Chem. Phys.* 1998, 108, 2940.
[50] Jiménez-Ángeles F.; Lozada-Cassou, M. paper in preparation (see [cond-mat/0303519](http://www.arxiv.org) at [http://www.arxiv.org](http://www.arxiv.org)).
[51] Lozada-Cassou M.; Díaz-Herrera, E. *J. Chem. Phys.* 1990, 93, 1386.
[52] Mier-y-Terán, L.; Díaz-Herrera, E.; Lozada-Cassou, M.; Saavedra-Barrera, R. *J. Comp. Phys.* 1989, 84, 326.
[53] Deserno M.; von Grünberg, H.-H. *Phys. Rev. E* 2002, 66, 011401.
[54] *Membranes Technology*, edited by S. P. Nunes and K.-V. Peinemann; Wiley-VCH, Weinheim, F. R. G., 2001.
[55] Blum, L. *Mol. Phys.* 1975, 30, 1529.
[56] Kazuo, H. *Mol. Phys.* 1977, 33, 1195.
[57] Lebowitz, J. L. *Phys. Rev.* 1964, 133, A895.