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A new method of deriving electrical double layer equations from electrolyte theories

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By assuming that one of the species of a liquid mixture is made of charged, planar walls of infinite extension such that its concentration tends to zero (here called the direct method), an electrical double layer theory is obtained from the Kirkwood and Poirier theory for ionic solutions. It is shown that this double layer theory is equivalent to the theory of Stillinger and Kirkwood. Another electrical double layer theory is obtained from the Kirkwood and Poirier theory by taking the limits of infinite radius and zero concentration in one of the species of a liquid mixture (here called the asymptotic method). It is shown that this theory is also equivalent to the Stillinger and Kirkwood theory and therefore the direct and the asymptotic methods are equivalent. This happens also when the hypernetted chain and mean spherical approximations are considered. Finally, the electrostatic interaction potential between a charged plate and an ion is discussed in view of its importance in the application of the direct and asymptotic methods.

I. INTRODUCTION

In interfacial systems, such as colloidal suspensions, biological membranes and electrodes, one of the phases is a solution containing free ions. For such systems an unequal distribution of positive and negative ions next to the interface is observed. This phenomenon, the so-called electrical double layer, has motivated a considerable amount of theoretical research, beginning with that of Gouy¹ and Chapman.²

In their theory, Gouy and Chapman (GC) solved the Poisson-Boltzmann equation for the following model: The ions are point charges, the solvent is a uniform dielectric medium everywhere in the solution, the solid phase is a hard, planar wall of infinite extension with uniform charged density on its surface, and the material from which the wall is made is assumed to have the same dielectric constant as that of the solvent. One of the obvious shortcomings of the GC theory is the neglect of the ion size effects. To some extent, Stern³ took these effects into account by assuming a distance of closest approach between the point ions and the wall. Therefore this theory separates the electric double layer into two regions: the inner Helmholtz layer, in which the ions interact with the wall as charged hard spheres; and the diffuse region, in which the GC theory is valid. Later on Grahame⁴ used Stern's theory to explain his experimental differential capacity data of a Hg-NaF interface, getting an excellent agreement between theory and experiment. Nevertheless it must be pointed out that Grahame did not obtain his calculated differential capacities entirely from theoretical bases.

After Grahame's work several authors assumed that the clue to the problem was in the structure of the inner double layer, and several semiphenomenological theories have appeared in the literature,⁵ however there seems to be gross inconsistencies between them.⁵ On the other hand, in dealing with interfacial problems several well fundamented statistical mechanical theories have been developed.⁶⁻¹² Even though these theories are mathematically and computationally difficult to handle, they allow a more systematic study of double layer sys-

tems and they are the more promising theories at present.

In constructing statistical mechanical theories for the problem of the electrical double layer at a charged, planar interface of infinite extension, two main procedures have been adopted in the literature, both essentially based on generalizations of existing electrolyte theories.

One of these methods [let us call it first principles method (FPM)] consists in the following steps: (a) The system of study is defined as a fluid formed by N charged particles (of n different species) immersed in a solvent of dielectric constant ϵ , and such that they are next to a hard, charged wall of infinite extension; the wall is regarded as an external field. (b) The interaction potential of this system U_N is constructed as

$$U_N = \sum_{i < j}^N U_{ij} + \sum_{i=1}^N U_i,$$

where U_{ij} is the interaction potential between the particles i and j and U_i is the interaction potential between the particle i and the external field. (c) Then pursuing one by one all the steps followed in the derivation of a given ionic solution theory, but with the new potential U_N , an electrical double layer theory is obtained. (d) Finally, in almost all the electrical double layer theories derived with this procedure, the potential U_i is taken to be^{8,10,11,12}

$$U_i = -\frac{4\pi e z_i \sigma}{\epsilon} x + A,$$

where e is the electronic charge, z_i is the valence of ion i , σ is the charge density on the wall, x is the perpendicular distance from the ion to the wall and A is an arbitrary constant which depends on the choice of zero potential. There is an exception in the case of the Stillinger-Kirkwood (SK) theory,⁶ where

$$U_i = -\frac{2\pi e z_i \sigma}{\epsilon} x + A,$$

which differs from the first expression only by a factor

of 2, but conceptually has important differences. In Sec. III we give a detailed discussion of these potentials.

Examples of the use of the FPM are, the SK theory, which is based on a generalization of the Kirkwood-Poirier (KP) theory¹³ for ionic solutions, and the Buff-Stillinger theory,¹⁰ which is based on a generalization of the cluster expansion approach (Mayer¹⁰). Other theories where the FPM has been used are the modified Poisson-Boltzmann theories^{8,12} and the Féat and Levine theory.¹¹

The other method used in the derivation of electrical double layer equations [let us call it asymptotic method (AM)], consist in the following steps: (a) The system of study is defined as a fluid formed by N small, charged particles (ions of n different species), next to a large spherical particle, uniformly charged on its surface, and such that the $N+1$ particles are immersed in a solvent of dielectric constant ϵ . (b) The interaction potential is given by

$$U_N = \sum_{i < j}^{N+1} U_{ij},$$

where U_{ij} is the interaction potential between the particles i and j . (c) Formally, with this total potential (U_N), there is no difference between the system described in (a) and an ionic solution. Therefore any of the existing ionic solution theories can be used to study this system. On the other hand, if the large sphere is sufficiently large, in principle it should be seen by the ions as a planar wall. Thus, by taking the limit of infinite radius and zero concentration for one of the species in a given ionic solution theory, one can obtain an electrical double layer theory. (d) Finally, it is to be noted that after the limit process the interaction potential between the large sphere and an ion, is given by

$$U_{Si} = -\frac{4\pi e z_i \sigma}{\epsilon} x + A,$$

where σ is the charge density on the surface of the large sphere, x is the perpendicular distance from the ion to the surface the large sphere and A is an arbitrary constant. Note that U_{iN+1} is to the AM as U_i to the FPM.

Examples of the use of the AM are the theories of Henderson and Blum,⁷ who applied this procedure to the hypernettedchain (HNC)¹⁴ and to the mean spherical (MS)¹⁴ approximations for ionic solutions.

These two methods (FPM and AM) are undoubtedly correct. However in the statistical mechanical theories of ionic solutions there is no restriction on the shape of the particles or the type of interaction among them.

Whence, one should be able to get an electrical double layer theory from any of the existing electrolyte theories, by simply assuming one of the ionic species as charged walls of infinite extension. Therefore we propose the following method [here called direct method (DM)] for the obtention of electrical double layer theories: (a) The system of study is defined as a fluid formed by N charged particles (ions of n different species), plus a charged, planar particle of infinite extension, and such that the $N+1$ particles are immersed in

a solvent of dielectric constant ϵ . (b) The interaction potential of the system is given by

$$U_{N+1} = \sum_{i < j}^{N+1} U_{ij},$$

where U_{ij} is the interaction potential between the particles i and j . (c) Formally, with this potential, any of the existing ionic solution theories can be used to study the system proposed in (a). Thus, we could take the final equations of a given ionic solution theory and assume one of the species in the solution as formed by charged, planar walls. Then, by taking the limit of zero concentration for this species, we obtain an electrical double layer theory. (d) The interaction potential between the charged plate and an ion is taken to be

$$U_{wall i} = -\frac{2\pi e z_i \sigma}{\epsilon} x + A,$$

where σ is the charge density on the surface of the wall-like particle, x is the distance from the ion i to the surface of the wall and A is an arbitrary constant. Note that $U_{wall i}$ is to the DM as U_i to the FPM.

If we compare the DM with the FPM we first notice that the FPM starts by considering a system of particles subject to the action of an external field, whereas in the DM there is not an external field acting on the particles of the system [step (a)]. Whence the DM and the FPM are conceptually different. Nevertheless, in the DM the total interaction potential of the system [step (b)] can be written as

$$U_{N+1} = \sum_{i < j}^{N+1} U_{ij} = \sum_{i < j}^N U_{ij} + \sum_{i=1}^N U_{iN+1},$$

where U_{iN+1} correspond to the potential $U_{wall i}$, given in the step (d) of the DM description. Therefore, if in the FPM the potential U_i of the interaction of an ion with the external field is taken to be equal to the $U_{wall i}$ of the DM (this is apparently true only for the SK theory), the DM and the FPM will be equivalent in the steps (a), (b), and (d). In the step (c), these two methods are clearly different. However, they should also be equivalent in this step, because, after all, the essential difference between these two methods is that in the DM the fact that in the electrolyte theories there are no restrictions on the shape of the particles of the system or type of interaction between them is used, and therefore we can simply substitute $U_{wall i}$ in the final equations of an electrolyte theory; whereas in the FPM this fact it is not considered, and therefore the potential U_i (correspondent to $U_{wall i}$) has to be carried out throughout all the steps followed in the construction of an electrolyte theory. Later we will show that these two methods are equivalent (although not equal).

If we compare the DM with the AM, we notice that in the step (a) the difference between them it is not only a matter of definition, but a more fundamental one. This is, due to the spherical shape of the large particle in the AM, when one takes the limit of infinite radius of this sphere the effect of autofield is lost, and an ion will interact with this sphere only as a test charge. In all the other steps the AM and the DM are also very different. Nevertheless, we shall show, by means of the

electroneutrality principle, that they are equivalent. However this equivalence might not hold for potentials different to the Coulombic (i.e., image potentials, polar, London, etc.), as we will comment in the conclusions.

In this work, we apply the DM and the AM to the KP theory to obtain two different electrical double layer theories. We show these two theories to be equivalent to each other. We reformulate the SK theory (which was obtained from the KP theory through the FPM) and we show that this theory is also equivalent to the double layer theories obtained from the KP theory with the AM and the DM. Also, we apply the DM to the HNC and MS approximations for ionic solutions and we obtain electrical double layer theories. We show these double layer theories to be equivalent to the theories previously obtained by Henderson and Blum⁷ by applying the AM to the HNC and MS approximations, respectively.

In Sec. IIA we apply the DM to the KP theory, and we show that the double layer equation obtained is equivalent to that obtained from the SK theory. In Sec. IIB we apply the AM to the KP theory and we obtain a double layer equation which is equivalent to those derived with the FPM (SK theory) and the DM. Therefore, in Sec. II we show that the three methods (FPM, AM, and DM) are equivalent when they are applied to the KP theory. In Sec. III the interaction potential between a charged wall and an ion is discussed, due to its fundamental role in the application of the three methods mentioned above. In Sec. IV, we apply the DM to the HNC and MS approximations and we show that the double layer equations obtained from these theories are equivalent to those previously derived from the same electrolytes theories by Henderson and Blum⁷ with the AM. Finally, in Sec. V some conclusions are presented.

II. EQUIVALENCE OF THREE DIFFERENT METHODS OF DERIVING AN ELECTRICAL DOUBLE LAYER THEORY FROM THE KP THEORY

A. Equivalence of the FPM and the DM

In this subsection we follow Kirkwood and Poirier¹³ to briefly introduce their ionic solution theory. Then, assuming that one of the ionic species considered in this theory is made of charged walls of infinite extension and taking the limit of zero concentration of this species (DM), we obtain an electrical double layer theory. Finally, we show this theory to be equivalent to the SK theory, which was obtained by applying the FPM to the KP theory.

Assuming the primitive model for an ionic solution and pairwise additivity for the interaction potential U_N of a system of N ions occupying a volume U , we have

$$U_N = \sum_{i < j=1}^N U^*(r_{ij}) + \sum_{i < j=1}^N U^{\text{el}}(r_{ij}), \quad (1)$$

where $U^*(r_{ij})$ and $U^{\text{el}}(r_{ij})$ are, respectively, the short and long range interaction potentials between the ions i and j , defined by

$$U^*(r_{ij}) = \begin{cases} \infty & r_{ij} < \frac{a_i + a_j}{2} \\ 0 & r_{ij} > \frac{a_i + a_j}{2} \end{cases} \quad (2)$$

and

$$U^{\text{el}}(r_{ij}) = \frac{Z_i Z_j e^2}{\epsilon r_{ij}}. \quad (3)$$

In Eqs. (2) and (3), a_i and a_j are the diameters of ions i and j , Z_i and Z_j their valences, e the electronic charge, the dielectric constant of the solvent, and r_{ij} the interionic distance.

Assigning to each ion i a charging parameter ζ_i ranging from zero to unity and defining the potential $U_N(\zeta_1 \dots \zeta_n)$ for a system in which each ion carries the charge $\zeta_i Z_i e$, a fraction of its full charge, we can write Eq. (1) as

$$U_N = U_N(0) + \zeta_1 \sum_{j=2}^n \zeta_j U^{\text{el}}(r_{1j}) + \zeta_1 U_{1,N-n}^{\text{el}}, \quad (4)$$

where

$$U_{1,N-n}^{\text{el}} = \sum_{j=n+1}^N \zeta_j U^{\text{el}}(r_{1j}), \quad (5)$$

and where the potential $U_N(0)$ is defined as the interaction potential of the N ions, when ion 1 is discharged ($\zeta_1 = 0$). On the other hand, as it is well known, the n -particles potential of the mean force, $W_N^{(n)}(1 \dots n)$ is given by

$$\exp[-\beta W_N^{(n)}(1 \dots n)] = \frac{\int_V \dots \int_V e^{-\beta U_N} dV_{n+1} \dots dV_N}{\int_V \dots \int_V e^{-\beta U_N} dV_1 \dots dV_N} \quad (6)$$

with

$$\beta = 1/kT,$$

where T is the temperature of the system and k is the Boltzmann constant. In writing Eqs. (1)–(6) we have not properly labeled the potentials $U^*(r_{ij})$, $U^{\text{el}}(r_{ij})$, and $W_N^{(n)}(1 \dots n)$, according to the species of the ions. This is to avoid excessive complication in the notation, but we will introduce a proper one in the final equations.

Substituting expression (4) into Eq. (6), using the theory of semi-invariants¹⁵ and after a clever algebraic manipulation, Kirkwood and Poirier¹³ were able to express the potential of the mean force $W_N^{(n)}(1 \dots n)$ as a power series in the charging parameter ζ_1 of ion 1. They obtained

$$W_N^{(n)}(1 \dots n) = W_N^{(n,0)}(1 \dots n) + \zeta_1 \sum_{j=2}^n \zeta_j U^{\text{el}}(r_{1j}) + \sum_{s=1}^{\infty} \frac{(-\beta)^{s-1}}{S!} \zeta_1^s [\Lambda_s^{(n)} - \Lambda_s^{(1)}], \quad (7)$$

where $W_N^{(n,0)}(1 \dots n)$ is the potential of the mean force acting on a set of n ions, when ion 1 is discharged. The quantities $\Lambda_s^{(n)}$ are cumulants of the electrostatic interactions involving ion 1. These cumulants are related to the moments $M_s^{(n)}$ through the relation¹³

$$M_s^{(n)} = \frac{(S-1)!}{(r-1)!(S-r)!} \Lambda_r^{(n)} M_{s-r}^{(n)}. \quad (8)$$

In turn, these moments are defined as¹³

$$M_s^{(n)} \equiv \langle [U_{1,N-n}^{(1)}]^S \rangle_{\zeta_1=0}^{(n)} = \frac{\int \cdots \int [U_{1,N-n}^{(1)}]^S e^{-\beta U_N^{(0)}} dV_{n+1} \cdots dV_N}{\int \cdots \int e^{-\beta U_N^{(0)}} dV_{n+1} \cdots dV_N}. \quad (9)$$

In order to apply the DM to the KP theory, we first notice that if $n \geq 2$, Eq. (7) can be rewritten as

$$W_N^{(n)}(1 \cdots n) = W_N^{(n,0)}(1 \cdots n) + \zeta_1 \left[\zeta_2 U^{(1)}(r_{12}) + \sum_{j=3}^n \zeta_j U^{(1)}(r_{1j}) \right] + \sum_{s=1}^{\infty} \frac{(-\beta)^{s-1}}{S!} \zeta_1^s [\Lambda_s^{(n)} - \Lambda_s^{(1)}] \quad (10)$$

and the moments $M_s^{(n)}$ can be written as

$$M_s^{(n)} = \langle [U_{1,N-n}^{(1)}]^S \rangle_{\zeta_1=0}^{(n)} \quad (n > 1) \quad (11)$$

and

$$M_s^{(1)} = \langle [U^{(1)}(r_{12}) + U_{1,N-2}^{(1)}]^S \rangle_{\zeta_1=0}^{(1)}. \quad (12)$$

Equations (7) and (10) are identical, except that in Eq. (10) we have explicitly written the interaction potential between the ions 1 and 2 and we have imposed the condition that $n \geq 2$. To proceed with our derivation, we observe that there is nothing in the KP theory which prevent us to assume that ion 2 has the form of a plate of infinite extension, uniformly charged on its surface. If we make this assumption the electrostatic interaction potential between the particle 2 and ion 1, is given by¹⁶

$$U^{(1)}(r_{12}) \equiv U^{(1)}(r_1) = -\frac{2\pi\sigma e Z_1}{\epsilon} r_1 + A, \quad (13)$$

where r_1 is the perpendicular distance from the surface of the plate (particle 2) to the center of ion 1, σ is the charge density on the plate and A is a constant which depends on the choice of zero potential. Equation (10) together with Eqs. (11)–(13) provides a formalism to calculate the distribution of ions next to a charged wall.

In order to compare our results with the SK theory let us introduce some new notation. That is, if $n \geq 2$ we can relabel the n particles over which the statistical average is taken, such that now particle 2 is called particle 0; ion 1 is called ion 1; ion 3 is called ion 2; ion 4 is called ion 3; ...; ion n is called ion m ($m > 0$, $m = n - 1$); ...; ion N is called ion M ($M = N - 1$). Therefore if $n \geq 1$, Eq. (5) can be expressed in terms of the index m , as

$$U_{1,N-n}^{(1)} = U_{1,M-m}^{(1)} = \sum_{j=m+1}^M \zeta_j U^{(1)}(r_{1j}) \quad (14)$$

and if $n = 1$, we can write

$$U_{1,N-n}^{(1)} = U^{(1)}(r_1) + U_{1,M-m}^{(1)}. \quad (15)$$

Whence from Eq. (14) the moments $M_s^{(n)}$ given by Eq. (11) can be expressed as

$$M_s^{(n)} = \langle [U_{1,M-m}^{(1)}]^S \rangle_{\zeta_1=0}^{(m)} \equiv M_s^{(m)} \quad (16)$$

and from Eq. (15), the moments $M_s^{(1)}$ given by Eq. (12) can be expressed as

$$M_s^{(n=1)} = \langle [U^{(1)}(r_1) + U_{1,M-1}^{(1)}]^S \rangle_{\zeta_1=0}^{(m=0)} \equiv \bar{M}_s. \quad (17)$$

Incorporating the new notation into Eq. (10), we get

$$W_M^{(m)}(1 \cdots m) = W_M^{(m,0)} + \zeta_1 \left[U^{(1)}(r_1) + \sum_{j=2}^m \zeta_j U^{(1)}(r_{1j}) \right] + \sum_{s=1}^{\infty} \frac{(-\beta)^{s-1}}{S!} \zeta_1^s [\Lambda_s^{(m)} - \bar{\Lambda}_s], \quad (18)$$

where $W_M^{(m)}(1 \cdots m)$ is the potential of the mean force for a set of m ions and a charged wall, the subindex M refers to the M ions in the system and $W_M^{(m,0)}$ is the potential of the mean force for a set of m ions and a charged wall when ion 1 is discharged. The cumulants $\Lambda_s^{(m)}$ and $\bar{\Lambda}$ are related to the moments $M_s^{(m)}$ and \bar{M} (respectively) through Eq. (8), provided that the change in notation is considered. Equation (18) has been previously obtained by Stillinger and Kirkwood⁶ following a similar but independent procedure to that used in the derivation of the KP theory (FPM).

On the other hand, if in Eq. (18) we assume the wall to be spherically shaped, the interaction potential between the wall and the ions will be given by Eq. (3) (spherical double layer system). Then assuming that the species corresponding to that of the wall is one of the ionic species in the solution, we recover Eq. (7). Therefore both formalisms, the KP and the SK, are equivalent and any of them can be properly applied to a pure electrolyte solution or to a double layer system (planar or spherical). Nevertheless, care must be taken in considering correctly the interaction potential between the particles of the system (we discuss this point in Sec. III).

To show, in a somewhat more explicit way, the simplicity of what we have here called DM, and the equivalence of the KP and SK theories; let us go back again to Eq. (7) of the KP theory and keep only the first term of the expansion ($S = 1$). Doing this and making $\zeta_i = 1$ for $i = 1, 2, \dots, n$ and $n = 2$, for simplicity, we get from Eq. (7),

$$W_N^{(2)}(1, 2) = W_N^{(2,0)} + U_{\alpha\beta}^{(1)}(r_{12}) + [M_1^{(2)} - M_1^{(1)}], \quad (19a)$$

where α and β refers to the species of ions 1 and 2, respectively. On the other hand, from Eqs. (5) and (9) we obtain

$$M_1^{(2)} = \frac{\sum_{j=3}^N \int U_{\alpha\beta}^{(1)}(r_{1j}) dV_j \int \cdots \int e^{-\beta U_N^{(0)}} dV_3 \cdots dV_{j-1} dV_{j+1} \cdots dV_N}{\int \cdots \int e^{-\beta U_N^{(0)}} dV_3 \cdots dV_N} \quad t = 1, 2, \dots, P, \quad (19b)$$

where P is the number of species in the solution. In Eq. (19b) we notice that all the terms in the summatory in which the ion j belongs to the same species t , are equal; whence defining the n -particles distribution function $g_{\alpha\ldots\nu}^{(n)}(1\ldots n; 0)$, for a set of n ions (of species $\alpha\ldots\nu$) in which ion 1 is discharged as

$$g_{\alpha\ldots\nu}^{(n)}(1\ldots n; 0) \equiv \exp[-\beta W_N^{(n,0)}] = \frac{V^n \int_{\mathbf{v}} \cdots \int_{\mathbf{v}} e^{-\beta U_N^{(0)}} dV_{n+1} \cdots dV_N}{\int_{\mathbf{v}} \cdots \int_{\mathbf{v}} e^{-\beta U_N^{(0)}} dV_1 \cdots dV_N}, \quad (20)$$

we obtain from Eq. (19b)

$$M_1^{(2)} = \frac{1}{g_{\alpha\beta}^{(2)}(r_{12}; 0)} \sum_{t=1}^P \rho_t \int_{\mathbf{v}} U_{\alpha t}^{\mathbf{e}1}(r_{13}) g_{\alpha\beta t}^{(3)}(1, 2, 3; 0) dV_3, \quad (21)$$

where ρ_t is the ionic concentration of the species t . In a similar manner we get

$$M_1^{(1)} = \frac{1}{g_{\alpha}^{(1)}(1; 0)} \left\{ \sum_{t=1}^P \rho_t \int_{\mathbf{v}} U_{\alpha t}^{\mathbf{e}1}(r_{13}) g_{\alpha t}^{(2)}(r_{13}; 0) dV_3 + \frac{1}{V} \int_{\mathbf{v}} U_{\alpha\beta}^{\mathbf{e}1}(r_{12}) g_{\alpha\beta}^{(2)}(r_{12}; 0) dV_2 \right\}. \quad (22)$$

Finally, defining the n -particle distribution function $g_{\alpha\ldots\nu}^{(n)}(1\ldots n)$ for a set of n ions as

$$g_{\alpha\ldots\nu}^{(n)}(1\ldots n) \equiv \exp[-\beta W_N^{(n)}(1\ldots n)] \quad (23)$$

and using Eqs. (8), (19a), (20), (21), and (22), we obtain

$$g_{\alpha\beta}^{(2)}(r_{12}) = g_{\alpha\beta}^{(2)}(r_{12}; 0) \exp \left\{ -\beta U_{\alpha\beta}^{\mathbf{e}1}(r_{12}) - \frac{\beta}{g_{\alpha\beta}^{(2)}(r_{12}; 0)} \sum_{t=1}^P \rho_t \int_{\mathbf{v}} U_{\alpha t}^{\mathbf{e}1}(r_{13}) \right. \\ \left. \times [g_{\alpha\beta t}^{(3)}(1, 2, 3; 0) - g_{\alpha\beta}^{(2)}(r_{12}; 0) g_{\alpha t}^{(2)}(r_{13}; 0)] dV_3 + \frac{\beta}{V} \int_{\mathbf{v}} U_{\alpha\beta}^{\mathbf{e}1}(r_{12}) g_{\alpha\beta}^{(2)}(r_{12}; 0) dV_2 \right\} \quad \alpha, \beta = 1, 2, \dots, P. \quad (24)$$

Equation (24) is the reformulated version (in terms of distribution functions) of the first term of the KP expansion. Following a similar procedure,¹⁷ from Eq. (18) we get a reformulated version of the SK expansion in terms of distribution functions. This is

$$g_{\alpha}^{(1)}(r_1) = g_{\alpha}^{(1)}(r_1; 0) \exp \left\{ -\beta U_{\alpha}^{\mathbf{e}1}(r_1) - \beta \sum_{q=1}^Q \rho_q \left[\frac{1}{g_{\alpha}^{(1)}(r_1; 0)} \int_{\mathbf{v}} U_{\alpha q}^{\mathbf{e}1}(r_{12}) g_{\alpha q}^{(2)}(r_1, r_2; 0) dV_2 \right. \right. \\ \left. \left. - \frac{1}{V} \int_{\mathbf{v}} \int_{\mathbf{v}} U_{\alpha q}^{\mathbf{e}1}(r_{12}) g_{\alpha q}^{(2)}(r_1, r_2; 0) dV_1 dV_2 \right] + \frac{\beta}{V} \int_{\mathbf{v}} U_{\alpha}^{\mathbf{e}1}(r_1) g_{\alpha}^{(1)}(r_1; 0) dV_1 \right\}, \quad \alpha = 1, 2, \dots, Q, \quad (25)$$

where $g_{\alpha}^{(1)}(r_1)$ is the one-particle distribution function for ion 1 of species α next to a wall, $g_{\alpha\ldots\nu}^{(m)}(r_1, r_2, \dots, r_m; 0)$ is the m -particle distribution function for a set of m ions next to a wall, when ion 1 is discharged, r_1, r_2, \dots, r_m are the perpendicular distances from the surface of the wall to the center of the ions 1, 2, \dots , m , and Q is the number of the ionic species in the solution.

To see the equivalence of Eqs. (24) and (25) (this is the equivalence between the DM and the FPM when applied to the KP theory) we first notice that in the absence of external fields other than that of the charged wall, in Eq. (25) the term

$$\frac{1}{V} \int_{\mathbf{v}} \int_{\mathbf{v}} U_{\alpha q}^{\mathbf{e}1}(r_{12}) g_{\alpha q}^{(2)}(r_1, r_2; 0) dV_1 dV_2 \equiv T$$

is constant and depends only on the relative position between ions 1 and 2. Therefore,

$$T = \int_{\mathbf{v}} U_{\alpha q}^{\mathbf{e}1}(r_{12}) g_{\alpha q}^{(2)}(r_{12}; 0) dV_2.$$

Substituting this relation into Eq. (25), we get

$$g_{\alpha}^{(1)}(r_1) = g_{\alpha}^{(1)}(r_1; 0) \exp \left\{ -\beta U_{\alpha}^{\mathbf{e}1}(r_1) - \beta \sum_{q=1}^Q \rho_q \left[\frac{1}{g_{\alpha}^{(1)}(r_1; 0)} \int_{\mathbf{v}} U_{\alpha q}^{\mathbf{e}1}(r_{12}) \right. \right. \\ \left. \left. \times [g_{\alpha q}^{(2)}(r_1, r_2; 0) - g_{\alpha}^{(1)}(r_1; 0) g_{\alpha q}^{(2)}(r_{12}; 0)] dV_2 + \frac{\beta}{V} \int_{\mathbf{v}} U_{\alpha}^{\mathbf{e}1}(r_1) g_{\alpha}^{(1)}(r_1; 0) dV_1 \right] \right\}, \quad \alpha = 1, 2, \dots, Q. \quad (26)$$

On the other hand assuming that in Eq. (24) the ion 2 of species β is a charged plate of infinite extension, $U_{\alpha\beta}^{\mathbf{e}1}(r_{12})$ becomes $U_{\alpha}^{\mathbf{e}1}(r_1)$, $g_{\alpha\beta}^{(2)}(r_{12})$ becomes $g_{\alpha}^{(1)}(r_1)$, and $g_{\alpha\beta t}^{(3)}(1, 2, 3; 0)$ becomes $g_{\alpha t}^{(2)}(r_1, r_2; 0)$ ($t=q$). Finally, if

we make $P=1+Q$ such that the species $1+Q=\beta$, and assuming $\rho_{\beta} \approx 0$, we get Eq. (26). Therefore, we have shown that by applying the DM to the KP theory one can easily obtain a double layer theory, and that this theory

is equivalent to the SK theory. This in turn was derived from the KP theory through what we have here called the FPM.

B. The asymptotic method (AM)

In this subsection we derive a double layer equation from the KP theory, by imagining that in an ionic solution the radius of one of its components becomes infinitely large while its concentration tends to zero (AM). We also show this equation to be equivalent to the double layer equations presented in the last subsection. Therefore here we show that within the KP formalism the AM, FPM, and DM are equivalent.

First let us assume that in Eq. (24), $p=1+Q$, such that the species $1+Q=\beta$ and $\rho_\beta \approx 0$. With this assumption and applying the superposition approximation to $g_{\alpha\beta i}^{(3)}(1, 2, 3; 0)$, Eq. (24) becomes

$$g_{\alpha\beta}^{(2)}(r_{12}) = g_{\alpha\beta}^{(2)}(r_{12}; 0) \exp \left\{ -\beta U_{\alpha\beta}^{(1)}(r_{12}) - \beta \sum_{i=1}^Q \rho_i \int U_{\alpha i}^{(1)}(r_{13}) g_{\alpha i}^{(2)}(r_{13}; 0) h_{\beta i}^{(2)}(r_{23}) dV_3 + \frac{\beta}{V} \int U_{\alpha\beta}^{(1)}(r_{12}) g_{\alpha\beta}^{(2)}(r_{12}; 0) dV_2 \right\} \quad \alpha = 1, 2, \dots, Q, \quad (27)$$

where

$$h_{\beta i}^{(2)}(r_{23}) = g_{\beta i}^{(2)}(r_{23}) - 1. \quad (28)$$

On the other hand, the charge ez_β of ion 2 of species β can be expressed in terms of the charge density σ on its surface as

$$ez_\beta = 4\pi R^2 \sigma,$$

where R is the radius of ion 2. Therefore,

$$U_{\alpha\beta}^{(1)}(r_{12}) = \frac{eZ_\alpha Z_\beta}{\epsilon r_{12}} = \frac{4\pi e R^2 \sigma Z_\alpha}{\epsilon r_{12}}. \quad (29)$$

Substituting Eq. (29) into Eq. (27), integrating in bipolar coordinates and defining

$$h_{\alpha i}^{(2)}(r_{13}; 0) = g_{\alpha i}^{(2)}(r_{13}; 0) - 1, \quad (30)$$

we find that

$$g_{\alpha\beta}^{(2)}(r_{12}) = g_{\alpha\beta}^{(2)}(r_{12}; 0) \exp \left\{ -\frac{2D_\alpha R^2}{\epsilon r_{12}} - \sum_{i=1}^Q L_{\alpha i} \int_0^\infty \int_{|r_{12}-r_{23}|}^{r_{12}+r_{23}} \frac{r_{23}}{r_{12}} h_{\beta i}^{(2)}(r_{23}) \times [h_{\alpha i}^{(2)}(r_{13}; 0) + 1] dr_{23} dV_{13} + C_1 \right\} \quad \alpha = 1, 2, \dots, Q, \quad (31)$$

where

$$D_\alpha = 2\pi\beta e Z_\alpha \sigma / \epsilon \quad (32)$$

and

$$L_{\alpha i} = 2\pi\beta e^2 Z_\alpha Z_i \rho_i / \epsilon. \quad (33)$$

C_1 is a constant equal to the last integral in the exponential of Eq. (27). Defining x and y as the radial distances from the surface of ion 2 to the center of ions 1 and 3, respectively, ($x \equiv r_{12} - R$ and $y \equiv r_{23} - R$), we obtain from Eq. (31),

$$g_{\alpha\beta}^{(2)}(x) = g_{\alpha\beta}^{(2)}(x; 0) \exp \left\{ -\frac{2D_\alpha R}{[1 + (x/R)]} - \sum_{i=1}^Q L_{\alpha i} \times \int_{-R}^\infty dy h_{\beta i}^{(2)}(y) \left[\int_{|x-y|}^{2R+x+y} \frac{(R+y)}{(R+x)} h_{\alpha i}^{(2)}(r_{13}; 0) dr_{13} + \frac{(R+y)}{(R+x)} (2R+x+y - |x-y|) \right] + C_1 \right\}. \quad (34)$$

Taking the limit $R \rightarrow \infty$ in this equation, we find

$$g_{\alpha}^{(1)}(x) = g_{\alpha}^{(1)}(x; 0) \exp \left\{ 2D_\alpha (x - R_\infty) - \sum_{i=1}^Q L_{\alpha i} \int_{-\infty}^\infty dy h_i^{(1)}(y) \times [K_{\alpha i}(x, y) + (2R_\infty + 3y - x - |x-y|)] + C_2 \right\}, \quad (35)$$

where

$$K_{\alpha i}(x, y) \equiv \int_{|x-y|}^\infty h_{\alpha i}^{(2)}(r_{13}; 0) dr_{13}, \quad (36)$$

and R_∞ and C_2 are an infinitely large constants obtained from R and C_1 , respectively, after the limit process. We point out that in taking this limit the functions $g_{\alpha\beta}^{(2)}(x)$, $g_{\alpha\beta}^{(2)}(x; 0)$, and $h_{\beta i}^{(2)}(y)$, which are two-particle distribution functions, become $g_{\alpha}^{(1)}(x)$, $g_{\alpha}^{(1)}(x; 0)$, and $h_i^{(1)}(y)$, respectively: these last three functions are one-particle distribution functions for an ion next to a charged wall. In Eq. (35) we see that the first term in the exponential diverges as $R \rightarrow \infty$. This is also the case of the term $(2R_\infty + 3y)$ which after the integration indicated in Eq. (35) becomes an infinite constant. All these constants are arbitrary to some extent and depend on the point of zero potential. Therefore we can choose them such that $g_{\alpha}^{(1)}(x) \rightarrow 1$ as $x \rightarrow \infty$. Whence Eq. (35) becomes

$$g_{\alpha}^{(1)}(x) = g_{\alpha}^{(1)}(x; 0) \exp \left\{ 2D_\alpha x - \sum_{i=1}^Q L_{\alpha i} \int_{-\infty}^\infty K_{\alpha i}(x, y) h_i^{(1)}(y) dy + \sum_{i=1}^Q L_{\alpha i} \int_0^\infty (x+y+|x-y|) h_i^{(1)}(y) dy \right\} \quad \alpha = 1, 2, \dots, Q. \quad (37)$$

where we have used the electroneutrality condition for a double layer system, namely,

$$\sigma = - \int_0^\infty \rho_{e1}(x) dx, \quad (38)$$

with

$$\rho_{e1}(x) \equiv \sum_{\alpha=1}^Q e Z_\alpha \rho_\alpha g_{\alpha}^{(1)}(x). \quad (39)$$

Equation (37) is the double layer equation obtained from the KP theory with the AM. To compare this equation with Eq. (26), we will rewrite Eq. (26) in a more convenient form. Therefore, substituting Eqs. (3) and (13) into Eq. (26), we obtain

$$g_{\alpha}^{(1)}(r_1) = g_{\alpha}^{(1)}(r_1; 0) \exp \left\{ D_\alpha (r_1 - A) - \sum_{\alpha=1}^Q \frac{L_{\alpha\alpha}}{2\pi g_{\alpha}^{(1)}(r_1; 0)} \times \int_0^\infty \frac{1}{r_{12}} [g_{\alpha\alpha}^{(2)}(r_1, r_2; 0) - g_{\alpha}^{(1)}(r_1; 0) g_{\alpha\alpha}^{(2)}(r_{12}; 0)] dV_2 + C_3 \right\}, \quad (40)$$

where C_3 is an infinite constant corresponding to the last integral in the exponential function of Eq. (26). Apply-

ing the superposition approximation to $g_{\alpha\alpha}^{(2)}(r_1, r_2; 0)$, identifying r_1 with x , r_2 with y , and t with q , and making some integrations in bipolar coordinates, Eq. (40) leads to

$$g_{\alpha}^{(1)}(x) = g_{\alpha}^{(1)}(x; 0) \exp \left\{ D_{\alpha}(x-A) - \sum_{t=1}^Q L_{\alpha t} \int_{-\infty}^{\infty} K_{\alpha t}(x, y) \times h_t^{(1)}(y) dy - \sum_{t=1}^Q L_{\alpha t} \int_0^{\infty} [B(y) - |x-y|] h_t^{(1)}(y) dy + C_3 \right\}, \quad (41)$$

where $B(y)$ is a function of the variable y , which becomes an infinite constant after integration. If we chose this constant together with constants A and C_3 such that $g_{\alpha}^{(1)}(x) \rightarrow 1$ as $x \rightarrow \infty$, we find

$$g_{\alpha}^{(1)}(x) = g_{\alpha}^{(1)}(x; 0) \exp \left\{ D_{\alpha}x - \sum_{t=1}^Q L_{\alpha t} \int_{-\infty}^{\infty} K_{\alpha t}(x, y) h_t(y) dy + \sum_{t=1}^Q L_{\alpha t} \int_0^{\infty} [y + |x-y|] h_t^{(1)}(y) dy \right\} \quad \alpha = 1, 2, \dots, Q. \quad (42)$$

Equations (37) and (42) are apparently different in the first and third terms of the exponentials. This is not really the case because using the electroneutrality condition given by Eq. (38), we notice that

$$D_{\alpha}x = -\frac{2\pi\beta e Z_{\alpha}}{\epsilon} \int_0^{\infty} x \rho_{\alpha 1}(y) dy. \quad (43)$$

Using this equation and after a trivial manipulation of Eq. (42) we obtain Eq. (37). Therefore we have shown that the double layer equation obtained from the KP theory with the AM is equivalent to those obtained with the FPM and DM. The use of Eq. (43) to show this equivalence will be further discussed in the following section.

III. ELECTROSTATIC INTERACTION

In the preceding section we obtained a double layer equation from the KP theory by assuming that in a mixture one of its components are charged plates of infinite extension while its concentration is approximately zero (the DM). Although this method is straightforward, care must be taken when considering the electrostatic interaction potential between the charged plate and an ion. We emphasize this point because there seems to be an interesting relation between this potential and the statistical average, over the system, of the long range interaction among the ions in the solution. In practically all the literature on the double layer problem the electrostatic interaction potential between a charged plate and a ion is taken to be^{7,9,10-12}

$$U_{\alpha}^{\text{el}}(x) = -\frac{4\pi e z_{\alpha} \sigma}{\epsilon} (x-A), \quad (44)$$

where all the parameters have been defined before. This expression can be obtained from the electrostatic theory by recognizing that inside the plate the electric field is zero. Therefore, applying Gauss' law to the plate, the electric field E outside the plate is given by

$$E = 4\pi\sigma/\epsilon, \quad (45)$$

and because

$$e z_{\alpha} E = -\partial U_{\alpha}^{\text{el}}(x)/\partial x, \quad (46)$$

we obtain Eq. (44). This equation can also be obtained by taking the limit of infinite radius of one of the ions, in the expression for the electrostatic potential between two ions (as in the case of the AM). Whence from Eq. (29),

$$\frac{4\pi R^2 \sigma e z_{\alpha}}{\epsilon r} = \frac{4\pi R^2 \sigma e Z_{\alpha}}{\epsilon R[1+(x/R)]} \xrightarrow{R \rightarrow \infty} -\frac{4\pi \sigma e z_{\alpha}}{\epsilon} (x-A). \quad (47)$$

Here we notice that due to the spherical geometry of the problem the effect of autofield is lost. That is, Eq. (44) is valid only in the case that the ion is considered as a *test charge*. However taking into account the effect on the wall due to the ion's electric field the expression for the electrostatic potential between the wall and the ion is given by¹⁸

$$U_{\alpha}^{\text{el}}(x) = \frac{1}{2} \int e z_{\alpha} \delta(x' - x) \phi_{\alpha}(x') dx', \quad (48)$$

where $\delta(x' - x)$ is the Dirac delta function and $\phi_{\alpha}(x')$ is given by Eq. (44). Therefore, integrating equation (48), we obtain

$$U_{\alpha}^{\text{el}}(x) = -\frac{2\pi e z_{\alpha} \sigma}{\epsilon} (x-A) \quad (49)$$

which differs from Eq. (44) by a factor of 2.

In the derivation of Eqs. (44) and (49) we have disregarded image potentials, which are of no interest here.

As it has been shown in the preceding section, we can obtain the SK theory (which was obtained through the FPM) by directly inserting Eq. (49) into the KP formalism and then taking the limit of zero concentration in one of the species in the solution (DM). On the other hand, if we take the limits of infinite radius and zero concentration in one of the ionic species in the KP theory (AM), we obtain expression (44) as the electrostatic potential between the plate and an ion, but also a correction term due to the statistical average over the system of the long range interaction between the ions in the solution [see Eqs. (29), (31), (34), (37), and (47)]. If we use the electroneutrality condition [Eq. (43)], this correction term cancels part of the potential (44) to give Eq. (49) [see Eqs. (37) and (42)], and the equivalence of the three methods can be shown.

Henderson and Blum⁷ have also found the need of this correction term to preserve the consistency of the Henderson-Abraham-Barker equations¹⁹ when applied to ionic solutions next to a charged wall. Therefore this correlation between a pure electrostatic situation and the statistical aspect of the problem, seems to be a general property of the distribution functions.

However, we wish to point out that the equivalence of the AM with the other two methods could only be shown through the electroneutrality condition, whereas this was not necessary in order to show the equivalence between the DM and the FPM. Therefore, it is possible that for some systems the AM would not be equivalent to the DM and the FPM (i.e., polar liquids, image potential, London forces) meanwhile the equivalence be-

tween the DM and the FPM does not have this restriction.

IV. HYPERNETED CHAIN AND MEAN SPHERICAL APPROXIMATIONS

In this section we extend the Ornstein-Zernike (OZ) equations to a double layer system, by applying the DM. In particular we discuss the HNC and MS approximations and compare our results with the double layer theories derived with the AM, by Henderson and Blum.⁷

The OZ equations for a multicomponent system is given by

$$h_{\alpha\beta}^{(2)}(r_{12}) = c_{\alpha\beta}^{(2)}(r_{12}) + \sum_{i=1}^P \rho_i \int h_{\alpha i}^{(2)}(r_{13}) c_{i\beta}^{(2)}(r_{23}) dV_3, \quad (50)$$

where $c_{\alpha\beta}^{(2)}(r_{12})$ is the two-particle direct correlation function for ions 1 and 2 of species α and β , respectively. All the other parameters have been already defined.

Assuming that in Eq. (50) the species α corresponds to charged plates of infinite extension and such that $\rho_\alpha \approx 0$, we obtain after integrating in bipolar coordinates

$$h_{\alpha\beta}^{(1)}(x) = c_{\alpha\beta}^{(1)}(x) + \sum_{i=1}^Q 2\pi\rho_i \int_{-\infty}^{\infty} h_{\alpha i}^{(1)}(y) dy \int_{|x-y|}^{\infty} s c_{i\beta}^{(2)}(s) ds$$

$$\beta = 1, 2, \dots, Q; \quad \alpha = P+1+Q, \quad (51)$$

where $s = r_{23}$; x and y are the perpendicular distances from the surface of the plate to the center of ions 2 and 3, respectively; and $h_{\alpha\beta}^{(1)}(x)$ and $c_{\alpha\beta}^{(1)}(x)$ are the total distribution function and the direct correlation function of an ion of species β next to a wall, respectively. Equations (51) are already the double layer version of the OZ equations. In order to be able to solve the OZ equations it is necessary to have an expression for $c_{\alpha\beta}^{(1)}(x)$ and $c_{i\beta}^{(2)}(s)$ in terms of $h_{\alpha\beta}^{(1)}(x)$ and $h_{i\beta}^{(2)}(s)$, respectively. In the theories of electrolytes the different approximations for $c_{\alpha\beta}^{(2)}(r_{12})$ are given as a function of $h_{\alpha\beta}^{(2)}(r_{12})$, $U_{\alpha\beta}^*(r_{12})$ (the short range potential), and $U_{\alpha\beta}^{\text{el}}(r_{12})$ (the electrostatic interaction between two ions) i.e.,

$$c_{\alpha\beta}^{(2)}(r_{12}) = f(h_{\alpha\beta}^{(2)}(r_{12}), U_{\alpha\beta}^*(r_{12}), U_{\alpha\beta}^{\text{el}}(r_{12})).$$

Therefore if we apply the DM to $c_{\alpha\beta}^{(2)}(r_{12})$, we obtain

$$c_{\alpha\beta}^{(2)}(r_{12}) \xrightarrow{\text{DM}} c_{\alpha\beta}^{(1)}(x) = f(h_{\alpha\beta}^{(1)}(x), U_{\alpha\beta}^*(x), U_{\alpha\beta}^{\text{el}}(x)), \quad (51a)$$

where $U_{\alpha\beta}^{\text{el}}(x)$ is given by Eq. (49) and $U_{\alpha\beta}^*(x)$ is the short range potential between the wall and the ions. Equations (51) and (51a) provide a very simple procedure to derive electrical double layer equations from the OZ type of electrolyte theories.

In order to make this procedure more explicit and to compare with previous works,⁷ let us rewrite Eqs. (51) in a different form. First let us assume that we have a solution (next to a charged wall) with only two species ($\beta = +, -$) and such that $\rho_+ = \rho_- = \frac{1}{2}\rho$, $|Z_+| = |Z_-| = Z$ and $a_+ = a_- = a$, where a_+ and a_- are the diameters of the ions of species (+) and (-), respectively. From Eqs. (51), we thus obtain that

$$h_{\alpha s}(x) = C_{\alpha s}(x) + 2\pi\rho \int_{-\infty}^{\infty} h_{\alpha s}(y) dy \int_{|x-y|}^{\infty} C_s(s) s ds, \quad (52)$$

and

$$h_{\alpha d}(x) = C_{\alpha d}(x) + 2\pi\rho \int_0^{\infty} h_{\alpha d}(y) dy \int_{|x-y|}^{\infty} C_d(s) s ds, \quad (53)$$

where

$$\begin{aligned} h_{\alpha s}(x) &= \frac{1}{2}[h_{\alpha+}^{(1)}(x) + h_{\alpha-}^{(1)}(x)], \\ h_{\alpha d}(x) &= \frac{1}{2}[h_{\alpha+}^{(1)}(x) - h_{\alpha-}^{(1)}(x)], \\ C_{\alpha s}(x) &= \frac{1}{2}[C_{\alpha+}^{(1)}(x) + C_{\alpha-}^{(1)}(x)], \\ C_{\alpha d}(x) &= \frac{1}{2}[C_{\alpha+}^{(1)}(x) - C_{\alpha-}^{(1)}(x)], \\ C_s(s) &= \frac{1}{2}[C_{++}^{(2)}(s) + C_{+-}^{(2)}(s)], \\ C_d(s) &= \frac{1}{2}[C_{++}^{(2)}(s) - C_{+-}^{(2)}(s)]. \end{aligned} \quad (54)$$

Defining

$$C_d^{\text{sr}}(s) \equiv C_d(s) + (q/s), \quad (55)$$

where

$$q \equiv \beta e^2 Z^2 / \epsilon,$$

Eq. (53) can be written as

$$\begin{aligned} h_{\alpha d}(x) &= C_{\alpha d}(x) + 2\pi\rho \int_0^{\infty} h_{\alpha d}(y) dy \int_{|x-y|}^{\infty} C_d^{\text{sr}}(s) s ds \\ &\quad + 2\pi\rho q \int_0^{\infty} h_{\alpha d}(y) [C + |x-y|] dy, \end{aligned} \quad (56)$$

where C is an arbitrary constant which depends on the zero potential point of the interaction between the plate and an ion. Introducing

$$C_{\alpha\beta}^{\text{sr}}(x) \equiv C_{\alpha\beta}^{(1)}(x) + U_{\alpha\beta}^{\text{el}}(x); \quad \beta = +, -, \quad (57)$$

where according with the DM, $U_{\alpha\beta}^{\text{el}}(x)$ is given by Eq. (49); we have

$$C_{\alpha d}(x) = C_{\alpha d}^{\text{sr}}(x) + \frac{2\pi\beta e z \sigma}{\epsilon} (x - A), \quad (58)$$

with

$$C_{\alpha d}^{\text{sr}}(x) \equiv \frac{1}{2}[C_{\alpha+}^{\text{sr}}(x) - C_{\alpha-}^{\text{sr}}(x)]. \quad (59)$$

Substituting Eq. (58) into Eq. (56) and choosing the constants A and C such that $h_{\alpha d}(x) \rightarrow 0$ as $x \rightarrow \infty$, we find that

$$\begin{aligned} h_{\alpha d}(x) &= C_{\alpha d}^{\text{sr}}(x) + \frac{2\pi\beta e z \sigma}{\epsilon} x + 2\pi\rho \int_0^{\infty} h_{\alpha d}(y) dy \int_{|x-y|}^{\infty} C_d^{\text{sr}}(s) s ds \\ &\quad + 2\pi\rho q \int_0^{\infty} h_{\alpha d}(y) (y + |x-y|) dy. \end{aligned} \quad (60)$$

Equations (52) and (60) are a reformulated version of Eqs. (51) for the double layer problem, in the special case of having a two-component solution of a symmetrical electrolyte. We point out that in its derivation no limit other than $\rho_\alpha \rightarrow 0$ has been taken. To compare our equations with those obtained by Henderson and Blum⁷ (with the AM), we rewrite Eq. (60) as

$$\begin{aligned} h_{\alpha d}(x) &= C_{\alpha d}^{\text{sr}}(x) + 2\pi\rho \int_0^{\infty} h_{\alpha d}(y) dy \int_{|x-y|}^{\infty} C_d^{\text{sr}}(s) s ds \\ &\quad + 2\pi\rho q \int_0^{\infty} h_{\alpha d}(y) [y - x + |x-y|] dy, \end{aligned} \quad (61)$$

where we have used the electroneutrality condition, expressed by

$$-\sigma = eZ\rho \int_0^\infty h_{\alpha d}(y) dy.$$

On the other hand in the MS approximation,

$$C_{\alpha d}^{sr}(x) = 0 \quad r > a, \quad (62)$$

and in the HNC approximation,

$$C_{\alpha d}^{sr}(x) = h_{\alpha d}(x) - \frac{1}{2} \{ \ln[g_{\alpha+}^{(1)}(x)] - \ln[g_{\alpha-}^{(1)}(x)] \}. \quad (63)$$

Substitution of Eq. (62) or (63) into Eqs. (52) and (61), gives the equations previously derived by Henderson and Blum.⁷ This result shows the equivalence of the AM and the DM in the HNC and MS approximations and suggest the possibility that any ionic solution theory may be extended to a double layer system with the DM. Nevertheless, we would like to point out that although both methods are equivalent, the direct correlation function $C_{\alpha d}(x)$ obtained with the DM is given by Eq. (58) while the one obtained by Henderson and Blum⁷ with the AM is given by

$$C_{\alpha d}(x) = C_{\alpha d}^{sr}(x) + \frac{4\pi\beta eZ\sigma}{\epsilon} x, \quad (64)$$

which differs from Eq. (58) by a factor of 2.

From the electrostatic point of view these two correlation functions are different because while in Eq. (64) the ions interact with the wall as *test charges*, in Eq. (58) the effect of the electric field produced by the ion, on the electric field produced by the wall is taken into account. However, when the AM is used to derive a double layer theory, an extra term appears as a consequence of the statistical average on the long range interaction between the ions of the system. Therefore by requiring that this theory satisfy the electroneutrality condition, a cancelation occurs and the equivalence of the AM and the DM can be shown. Nevertheless, this cancelation may not take place when considering different types of interaction among the particles of a system (i.e., polar liquids) and in that case the two methods may not be equivalent, but this is a controversial point.

V. CONCLUSIONS

In the electrolyte theories there are not restrictions on the type of potential between the particles of the system. Using this fact, in this work we have presented a straightforward procedure for the obtention of electrical double layer theories from electrolyte theories (here called direct method). Within the framework of the KP theory, we showed the direct method to be equivalent to other two methods previously used in the literature, namely, the first principles method and the asymptotic method. Also, within the framework of the HNC and MS approximations we showed that the direct and the asymptotic methods are equivalent. From these results, we believe it is safe to assume that in general a double layer theory derived from any ionic solutions theory with the direct method, and that this theory would be equivalent to that derived from the same electrolyte theory with the asymptotic method. However, we point out that we were able to show this equivalence only by

means of the electroneutrality principle. Therefore, for other types of potentials (i.e., image potential, polar liquids, etc.), this equivalence may not hold.

On the other hand, among the different electrical double layer theories which have been obtained in the literature with the first principles method, there are some which took the electrostatic interaction potential between the wall and an ion as that of a wall and a test charge^{8,10,11,12} whereas in others the effect of the ion's electric field on the wall (autofield effect) was considered.⁶ In the direct method the effect of autofield is considered. Therefore, we expect that as long as the autofield's effect is considered in the ion wall electrostatic potential, the direct method and the first principles method will be equivalent in deriving electrical double layer equations. Finally, as the application of the direct method is so straightforward, we believe this method provides a simple procedure to study more complex systems as for example the interaction of two planar double layers (of interest in colloid chemistry).

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¹G. Gouy, J. Phys. 9, 457 (1910).

²D. L. Chapman, Philos. Mag. 25, 475 (1913).

³O. Stern, Z. Elektrochem. 30, 508 (1934).

⁴D. C. Grahame, J. Am. Chem. Soc. 76, 4819 (1954); 79, 2093 (1957).

⁵J. O'M. Bockris, M. A. V. Devanathan, and K. Muller, Proc. R. Soc. A 274, 55 (1963).

⁶F. H. Stillinger and J. G. Kirkwood, J. Chem. Phys. 33, 1282 (1960).

⁷D. Henderson and L. Blum, J. Chem. Phys. 69, 5441 (1978); J. Electroanal. Chem. 93, 151 (1978); D. Henderson, L. Blum, and W. R. Smith, Chem. Phys. Lett. 63, 381 (1979).

⁸C. W. Outhwaite, J. C. S. Faraday II 74, 1214 (1978); Chem. Phys. Lett. 7, 636 (1970); S. Levine and C. W. Outhwaite, J. C. S. Faraday II 74, 1670 (1978).

⁹L. Blum, J. Phys. Chem. 81, 136 (1977).

¹⁰F. P. Buff and F. H. Stillinger, J. Chem. Phys. 37, 1 (1962); 39, 1911 (1963); J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (Wiley, New York, 1940).

¹¹G. R. Féat and S. Levine, J. C. S. Faraday II 73, 1345 (1977); 73, 1359 (1977).

¹²G. M. Bell and S. Levine, in *Chemical Physics of Ionic Solutions*, edited by B. E. Conway and R. G. Barradas (Wiley, New York, 1964).

¹³J. G. Kirkwood and J. C. Poirier, J. Phys. Chem. 58, 591

(1954).

¹⁴See, for example, D. A. McQuarrie, *Statistical Mechanics* (Harper & Row, New York, 1976).

¹⁵H. Cramer, *Mathematical Methods of Statistics* (Princeton University, Princeton, New Jersey, 1946).

¹⁶A detailed discussion on this potential is given in the Sec. III of this work.

¹⁷Marcelo Lozada Cassou, "Statistical Mechanics of Model Charged Systems," Universidad Autónoma Metropolitana, Iztapalapa, México, D.F., México, internal report, 1980.

¹⁸J. D. Jackson, *Classical Electrodynamics* (Wiley, New York, 1962).

¹⁹D. Henderson, F. F. Abraham, and J. A. Barker, *Mol. Phys.* 31, 1291 (1976).