

The structure of electrolytes at charged surfaces: The primitive model

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The effects of ion size on the structure of a primitive model electrical double layer at a charged surface is considered using the integral equation method based on a combined hypernetted chain and mean spherical approximation (HNC/MSA). The HNC/MSA is shown to be a nonlinear weak field approximation. The contact values of the surface ion distribution functions are shown to have the correct quadratic dependence on the surface charge density. An analytical comparison between the HNC/MSA and earlier work based on the modified Poisson-Boltzmann equation is given.

I. INTRODUCTION

In the past, theoretical studies of the behavior of an electrolyte at a charged surface has been based on modifying the Poisson-Boltzmann equation using the potential approach.¹ Very recently, the integral equation method of liquid state physics has been applied to study the electrical double layer.² While the integral equation method enjoyed reasonable success in predicting bulk fluid properties, its ability to handle nonuniform fluids and its relationship to the potential approach had not been well established.

In this paper we study the structure of a restricted primitive model (RPM) electrolyte at a charged surface. Our approach is equivalent to using the hypernetted chain (HNC) closure for the surface-ion direct correlation functions and the mean spherical approximation (MSA) for the bulk ion-ion correlation functions. Contrary to a conjecture by Henderson *et al.*,² we have shown that the HNC closure alone is sufficient to give the correct asymptotic behavior of the total ionic density at the surface in the limit of high surface charge. The use of the MSA allows us to extract analytic results in the limit of low ionic densities from which we can establish explicitly the connection between the integral equation method and the potential approach.

In the RPM the ions are treated as equal size hard spheres of diameter R with embedded point charges of valence Z_i in the center. The solvent is taken to be an inert continuum that provides a uniform dielectric constant ϵ . The charged surface is a smooth impenetrable planar half-space with a uniform charge density σ . It is formally constructed by first considering a large ion of diameter R_0 , valence Z_0 , and then taking the limit $R_0 \rightarrow \infty$, $Z_0 \rightarrow \infty$ but with $\sigma = (Z_0 e / \pi R_0^2)$ finite. Effects such as dielectric saturation and image interactions have been omitted because we consider such effects to be outside the realm of a primitive model electrolyte. A proper treatment of these effects would require going beyond the primitive model when the solvent molecules and the ions can be then treated on an equal basis—as discrete particles.

In the next section we give a formal derivation of an equation for the one-particle density distribution function of nonuniform fluids. From this result we can see the exact status of the HNC closure and the possibilities

of going beyond this approximation. We shall also give the result for the HNC number densities at contact with the surface. In Sec. III we examine the HNC/MSA in detail and establish its relation to earlier work. Numerical results such as the ionic density profiles, the surface charge-surface potential relationship and the double layer capacitance will be given in Sec. IV. The paper closes with a short conclusion.

II. ONE PARTICLE DENSITY DISTRIBUTION—HNC

Consider a system of particles $\{N_i\} = \{N_1, N_2, \dots\}$, where N_i is the number of particles of component i . The Hamiltonian for this system in an external field is

$$H(\{N_i\} | \lambda) = H_0(\{N_i\}) + \lambda \int d\mathbf{r} \sum_j \phi_j(\mathbf{r}) \hat{\rho}_j(\mathbf{r}), \quad (2.1)$$

where $\phi_j(\mathbf{r})$ is the interaction between a particle of species j at \mathbf{r} with the external field which vanishes in the limit $r \rightarrow \infty$. The density operator for component j is

$$\hat{\rho}_j(\mathbf{r}) = \sum_{\alpha=1}^{N_j} \delta(\mathbf{r} - \mathbf{r}_j^{(\alpha)}). \quad (2.2)$$

The coupling parameter λ is a formal device by which the external field can be varied continuously. The limit $\lambda = 0$ corresponds to a uniform bulk fluid with Hamiltonian $H_0(\{N_i\})$ and the external field is at full strength at $\lambda = 1$. If the system is in equilibrium with a bulk fluid at uniform concentration ρ_i and chemical potential μ_i , the thermodynamic potential $\Omega(\lambda)$, for the system in an external field is given by ($\beta = 1/kT$)

$$\exp[-\beta\Omega(\lambda)] = \sum_{\{N_i\}} \frac{h^{-3\sum_i N_i}}{\prod_i N_i!} \exp\left(\beta \sum_i \mu_i N_i\right) \times \int d\mathbf{r} d\mathbf{p} \exp[-\beta H(\{N_i\} | \lambda)]. \quad (2.3)$$

By differentiating with respect to λ , we can show that

$$\frac{\partial \Omega(\lambda)}{\partial \lambda} = \int d\mathbf{r} \sum_i \rho_i(\mathbf{r} | \lambda) \phi_i(\mathbf{r}) \quad (2.4)$$

and

$$\frac{\partial \rho_i(\mathbf{r} | \lambda)}{\partial \lambda} = -\beta \int d\mathbf{s} \sum_j \phi_j(\mathbf{s}) \times \langle [\hat{\rho}_j(\mathbf{s}) \hat{\rho}_i(\mathbf{r})] - \langle \hat{\rho}_j(\mathbf{s}) \rangle \langle \hat{\rho}_i(\mathbf{r}) \rangle \rangle, \quad (2.5)$$

where

$$\rho_i(\mathbf{r}|\lambda) = \langle \hat{\rho}_i(\mathbf{r}) \rangle \quad (2.6)$$

is the number density of component i and $\langle \rangle$ denotes the ensemble average taken with respect to $H(\{N_i\}|\lambda)$. Using the definition of the pair distribution function $g_{ij}(\mathbf{r}, \mathbf{s}|\lambda)$ between species i and j :

$$\rho_i(\mathbf{r}|\lambda) g_{ij}(\mathbf{r}, \mathbf{s}|\lambda) \rho_j(\mathbf{s}|\lambda) = \langle \hat{\rho}_i(\mathbf{r}) \hat{\rho}_j(\mathbf{s}) \rangle - \rho_i(\mathbf{r}|\lambda) \delta_{ij} \delta(\mathbf{r} - \mathbf{s}) ; \quad (2.7)$$

we can rewrite Eq. (2.5) as

$$\frac{\partial \ln \rho_i(\mathbf{r}|\lambda)}{\partial \lambda} = -\beta \left(\phi_i(\mathbf{r}) + \int d\mathbf{s} \sum_j \phi_j(\mathbf{s}) \rho_j(\mathbf{s}|\lambda) h_{ij}(\mathbf{r}, \mathbf{s}|\lambda) \right), \quad (2.8)$$

where

$$h_{ij}(\mathbf{r}, \mathbf{s}|\lambda) = g_{ij}(\mathbf{r}, \mathbf{s}|\lambda) - 1. \quad (2.9)$$

Now we can use the nonuniform Ornstein-Zernike equation

$$h_{ij}(\mathbf{r}, \mathbf{s}|\lambda) = c_{ij}(\mathbf{r}, \mathbf{s}|\lambda) + \sum_k \int dt c_{ik}(\mathbf{r}, \mathbf{t}|\lambda) \times \rho_k(\mathbf{t}|\lambda) h_{kj}(\mathbf{t}, \mathbf{s}|\lambda) \quad (2.10)$$

to recast Eq. (2.8) in terms of a nonuniform direct correlation function $c_{ij}(\mathbf{r}, \mathbf{s}|\lambda)$,

$$\ln \left(\frac{\rho_i(\mathbf{r})}{\rho_i} \right) = -\beta \phi_i(\mathbf{r}) + \int_0^1 d\lambda \int d\mathbf{s} \sum_j c_{ij}(\mathbf{r}, \mathbf{s}|\lambda) \frac{\partial \rho_j(\mathbf{s}|\lambda)}{\partial \lambda}, \quad (2.11)$$

with

$$\rho_i(\mathbf{r}) \equiv \rho_i(\mathbf{r}|\lambda=1). \quad (2.12)$$

Since we have not made any approximations, Eq. (2.11) is therefore exact. A similar result has been derived by Saam and Ebner using the density functional method.⁴

To proceed further we need to have some knowledge of the nonuniform direct correlation function $c_{ij}(\mathbf{r}, \mathbf{s}|\lambda)$. We anticipate $c_{ij}(\mathbf{r}, \mathbf{s}|\lambda)$ to be a short ranged function of \mathbf{r}, \mathbf{s} and $|\mathbf{r} - \mathbf{s}|$. Provided the external field is not too strong a very plausible approximation is

$$c_{ij}(\mathbf{r}, \mathbf{s}|\lambda) \approx c_{ij}(\mathbf{r}, \mathbf{s}|\lambda=0) = c_{ij}^{\text{bulk}}(|\mathbf{r} - \mathbf{s}|). \quad (2.13)$$

Due to the short ranged nature of $c_{ij}(\mathbf{r}, \mathbf{s}|\lambda)$, the approximation to replace it by the bulk direct correlation function $c_{ij}^{\text{bulk}}(|\mathbf{r} - \mathbf{s}|)$ is expected to be much less serious than a similar approximation on the longer ranged indirect correlation function $h_{ij}(\mathbf{r}, \mathbf{s}|\lambda)$. We note that the use of Eq. (2.13) for the electrical double layer problem automatically neglects image interactions.¹ However, as we have stated in the Introduction, we cannot study such effects properly within the primitive model.

Combining Eqs. (2.11) and (2.13), we get

$$\ln \left(\frac{\rho_i(\mathbf{r})}{\rho_i} \right) = -\beta \phi_i(\mathbf{r}) + \int d\mathbf{s} \sum_j c_{ij}^{\text{bulk}}(|\mathbf{r} - \mathbf{s}|) [\rho_j(\mathbf{s}) - \rho_j]. \quad (2.14)$$

For the electrical double layer problem, the external field ϕ_i is due to the presence of the charged surface—treated initially as a large spherical particle of diameter R_0 . Consequently, we can immediately recognize Eq. (2.14) as the Ornstein-Zernike equation for the sur-

face-ion indirect correlation function with an HNC closure for the surface-ion direct correlation function. We note that the form of c_{ij}^{bulk} has been left unspecified. If the exact bulk direct correlation function is known (e.g., from machine simulations) it can be used in Eq. (2.14); otherwise any reasonable approximate representation of c_{ij}^{bulk} may be used and this will constitute a further approximation.

For an electrical double layer at a planar interface, we need to reduce Eq. (2.14) to a one dimensional form. The potential $\phi_i(\mathbf{r})$ contains a hard core part which ensures

$$\rho_i(\mathbf{r}) = 0, \quad r < R_{i0} \equiv \frac{1}{2}(R + R_0). \quad (2.15)$$

For $r > R_{i0}$, $\phi_i(\mathbf{r})$ is the Coulomb potential; hence, Eq. (2.14) becomes

$$\ln \left(\frac{\rho_i(r)}{\rho_i} \right) = -\frac{\beta Z_i Z_0 e^2}{\epsilon r} + \int d\mathbf{s} \sum_j c_{ij}(|\mathbf{r} - \mathbf{s}|) \times [\rho_j(\mathbf{s}) - \rho_j], \quad r > R_{i0}. \quad (2.16)$$

In the planar limit $R_0 \rightarrow \infty$, the divergence in the first term of Eq. (2.16) is exactly canceled by a similar divergence in the second term. To demonstrate this we make the formal decomposition

$$c_{ij}^{\text{bulk}}(|\mathbf{r} - \mathbf{s}|) = -\frac{\beta Z_i Z_j e^2}{\epsilon |\mathbf{r} - \mathbf{s}|} + c_{ij}^0(\mathbf{r} - \mathbf{s}), \quad 0 < |\mathbf{r} - \mathbf{s}| < \infty, \quad (2.17)$$

where c_{ij}^0 is now a short ranged function. Combining Eqs. (2.16) and (2.17) together with the bulk electroneutrality condition

$$\sum_i \rho_i Z_i = 0, \quad (2.18)$$

we get, after doing the angular integrations,

$$\ln \left(\frac{\rho_i(s)}{\rho_i} \right) = -\left(\frac{\beta Z_i e^2}{\epsilon r} \right) \left\{ Z_0 + \int d\mathbf{s} \sum_j Z_j \rho_j(s) \right\} - \frac{4\pi\beta Z_i e^2}{\epsilon} \int_r^\infty ds s \left(1 - \frac{s}{r} \right) \sum_j Z_j \rho_j(s) + \int d\mathbf{s} \sum_j c_{ij}^0(|\mathbf{r} - \mathbf{s}|) [\rho_j(\mathbf{s}) - \rho_j]. \quad (2.19)$$

The term in large curly brackets vanishes because the charge in the diffuse double layer must balance the surface charge, that is,

$$Z_0 = -\int d\mathbf{s} \sum_j Z_j \rho_j(s). \quad (2.20)$$

We can now safely take the planar limit $R_0 \rightarrow \infty$, $Z_0 \rightarrow \infty$ with constant surface charge density $\sigma = Z_0 e / \pi R_0^2$, by changing to one dimensional variables $x = r - R_{i0}$, $y = s - R_{i0}$ and by defining the surface-ion indirect correlation function

$$h_i(x) = [\rho_i(x + R_{i0}) / \rho_i] - 1, \quad (2.21)$$

so that Eqs. (2.15) and (2.19) become

$$h_i(x) = -1, \quad x < 0, \quad (2.22)$$

$$\ln[1 + h_i(x)] = -\beta Z_i e \psi(x) + \sum_j \rho_j \int_{-\infty}^{\infty} dy c_{ij}^0(|x - y|) \times h_j(y), \quad x > 0, \quad (2.23)$$

where

$$c_{ij}^0(x) = 2\pi \int_x^\infty ds s c_{ij}^0(s) \quad (2.24)$$

and

$$\psi(x) = \frac{4\pi}{\epsilon} \int_x^\infty dy(x-y) \sum_j \rho_j Z_j e h_j(y) \quad (2.25)$$

is the mean electrostatic potential. It is easy to verify that $\psi(x)$ satisfies the one dimensional Poisson equation subjected to the boundary conditions [cf. Eq. (2.20)]

$$\frac{d\psi}{dx} \Big|_{x=0} = -\frac{4\pi\sigma}{\epsilon} = \frac{4\pi}{\epsilon} \int_0^\infty dy \sum_j \rho_j Z_j e h_j(y), \quad (2.26)$$

$$\psi(x) \rightarrow 0, \text{ as } x \rightarrow \infty. \quad (2.27)$$

The Poisson-Boltzmann result is a special limit of Eq. (2.23) with $c_{ij}^0 = 0$, which is a good approximation at low ionic densities.⁵

From Eq. (2.23) it is possible to derive the following result for the contact values of $h_i(x)$ (see Appendix),

$$kT \sum_i \rho_i [1 + h_i(0)] = \frac{1}{2} \left(kT \sum_i \rho_i + \chi^{-1} \right) + \frac{\epsilon E^2}{8\pi}, \quad (2.28)$$

where $E = 4\pi\sigma/\epsilon$, and χ is the isothermal compressibility of the restricted primitive model electrolyte given by

$$\chi = \frac{-1}{V} \left(\frac{\partial V}{\partial P} \right)_T = \beta \left(\sum_i \rho_i - \sum_{i,j} \rho_i \rho_j \int d\mathbf{r} c_{ij}^0(r) \right)^{-1}. \quad (2.29)$$

Equation (2.28) should be compared with the exact result⁶ which also neglects image interactions

$$kT \sum_i \rho_i [1 + h_i(0)] = P + \frac{\epsilon E^2}{8\pi}, \quad (2.30)$$

and with the Poisson-Boltzmann result which approximates the pressure of the bulk electrolyte P in Eq. (2.30) by the ideal gas limit $kT \sum_i \rho_i$. Contrary to the conjecture by Henderson *et al.*,² who used the HNC- c_{ij}^0 , the contact value at zero field should be $\frac{1}{2} (kT \sum_i \rho_i + \chi_{\text{HNC}}^{-1})$ and not $(kT \sum_i \rho_i / \chi_{\text{HNC}})^{1/2}$. Furthermore, the HNC surface-ion closure alone, independent of the choice for c_{ij}^0 , is sufficient to guarantee the correct asymptotic quadratic dependence of the contact values on the surface charge density. This suggests that the failure of the HNC/HNC result² to obey the E^2 dependence is probably due to problems associated with having to cancel numerically the divergence discussed under Eq. (2.16). Finally, we note that the E^2 dependence is only a consequence of the long ranged nature of the Coulomb potential and electroneutrality so that the exact result, Eq. (2.30), does not appear to be a very severe test of various approximate theories of the electrical double layer.

Now in order to go beyond the HNC surface-ion closure, we need to return to Eq. (2.11) and find a closure for $c_{ij}(r, s | \lambda)$ that is better than the approximation given by Eq. (2.13) which is limited to low or moderate surface charge densities.

III. HNC/MSA ELECTRICAL DOUBLE LAYER

In lieu of an exact form for the short ranged part of the bulk ionic direct correlation c_{ij}^0 , we shall need an

approximate representation. We have already mentioned that the choice $c_{ij}^0 = 0$ reduces to the Poisson-Boltzmann theory which neglects ionic size. Restricting ourselves to 1:1 electrolytes, we know that both the MSA and HNC approximation give good descriptions of bulk electrolyte thermodynamics so that we have two possible candidates for c_{ij}^0 . Although the HNC is superior at high electrolyte concentrations,⁷ in the concentration range of relevance to colloid and surface chemistry (≤ 0.5 mole dm^{-3}) the difference in bulk thermodynamic properties predicted by the MSA and HNC is small. However, the MSA c_{ij}^0 is also known analytically, so it has the advantage from a pedagogical viewpoint since the physical content of the HNC/MSA approximation can be exhibited explicitly and the cancellation of divergent terms, discussed under Eq. (2.16), can also be carried out analytically. Neither of these advantages are available to the HNC/HNC theory since the analytic form of the HNC- c_{ij}^0 is not known and the divergent terms have to be handled numerically.² Bearing these remarks in mind we now consider in detail the effects of finite ion size on the structure of the electrical double layer based on the HNC/MSA.

Using the MSA form for c_{ij}^0 , Eq. (2.23) becomes

$$\ln[1 + h_i(x)] = -\beta Z_i e \psi(x) + \sum_j \rho_j \int_{x-R}^{x+R} dy c_{ij}^{\text{MSA}}(|x-y|) \times h_j(y), \quad x > 0, \quad (3.1)$$

where

$$c_{ij}^{\text{MSA}}(x) = e^{\text{PYHS}}(x) + Z_i Z_j e^c(x). \quad (3.2)$$

$e^{\text{PYHS}}(x)$ is obtained from the solution of the Percus-Yevick hard sphere fluid⁸

$$e^{\text{PYHS}}(x) = \begin{cases} \frac{\pi R^2}{(1-\eta)^4} \left[-\frac{1}{5} \eta(1+2\eta)^2 \left(1 - \frac{x^5}{R^5}\right) + \eta(\eta+2)^2 \left(1 - \frac{x^3}{R^3}\right) - (1+2\eta)^2 \left(1 - \frac{x^2}{R^2}\right) \right], & x < R, \\ 0, & x > R, \end{cases} \quad (3.3)$$

with

$$\eta = \frac{\pi R^3}{6} \sum_i \rho_i. \quad (3.4)$$

$e^c(x)$ is given by⁷

$$e^c(x) = \begin{cases} \frac{2\pi\beta e^2}{\epsilon} R \left[\frac{B^3}{3} \left(1 - \frac{x^3}{R^3}\right) - B \left(1 - \frac{x^2}{R^2}\right) + \left(1 - \frac{x}{R}\right) \right], & x < R, \\ 0, & x > R, \end{cases} \quad (3.5)$$

where

$$B = (1 + \kappa R - (1 + 2\kappa R)^{1/2}) / \kappa R, \quad (3.6)$$

and κ is the inverse Debye screening length

$$\kappa^2 = \frac{4\pi\beta e^2}{\epsilon} \sum_i \rho_i Z_i^2. \quad (3.7)$$

Equations (3.1)–(3.7) together with Eqs. (2.22), (2.25), and (2.26) constitute the HNC/MSA treatment of the electrical double layer. The solution of these equations will give the relation between the surface charge and surface potential at the planar interface.

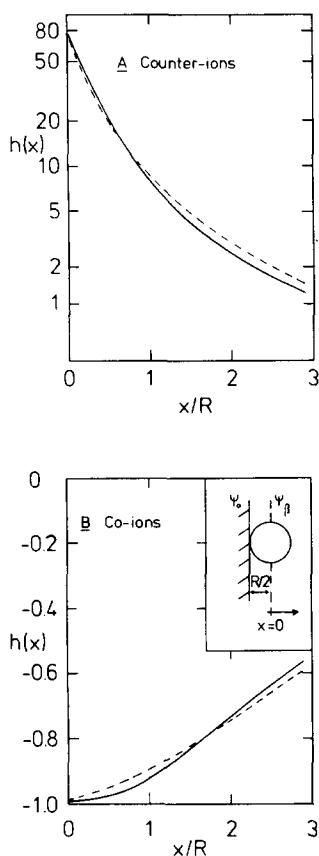


FIG. 1. Total surface-ion correlation function for (A) counter-ions and (B) co-ions of a restricted primitive model electrolyte of bulk concentration $0.1 \text{ mole, dm}^{-3}$, ionic diameter $R = 4.25 \text{ \AA}$, near a surface with charge density 0.16 C cm^{-2} ($T = 298 \text{ K}$, $\epsilon = 78.5$). Present work (HNC/MSA): (—) Poisson-Boltzmann+Stern layer (PB+S); (---). For counter-ions an arcsinh vertical scale is used.

The potential at the charged surface ψ_0 , and the potential at the plane of closest approach of the ions $\psi_\beta \equiv \psi(x=0)$ (see Fig. 1) are related by

$$\psi_0 = \psi_\beta + 2\pi\sigma R/\epsilon. \quad (3.8)$$

We shall compare our results with those of the Poisson-Boltzmann theory plus a Stern layer correction (PB+S).⁹ In the PB+S theory, finite ion size effects are accounted for by defining a region adjacent to the surface of one radius thick from which all (point) ions are excluded. In this case, ψ_β is given by

$$\psi_\beta = (2kT/e) \operatorname{arcsinh}(2\pi\sigma/\epsilon\kappa kT). \quad (3.9)$$

In order to demonstrate explicitly the difference between the HNC/MSA and PB+S theories, we observe that the left-hand side of Eq. (3.1) is by definition proportional to the potential of mean force $W_i(x)$ between an ion of type i and the charged surface. Using the known MSA expressions for e_i^0 , we can obtain a density expansion for $W_i(x)$ in terms of the bulk density of the electrolyte:

$$W_i(x) = Z_i e\psi(x) + W_i^{(2a)}(x) + W_i^{(2b)}(x) + W_i^{(3)}(x) + \dots, \quad (3.10)$$

where

$$W_i^{(2a)}(x) = \int_x^\infty dx' \left(\int_A dA \cdot \hat{x} \rho^{\text{NUM}}(x') kT \right), \quad (3.11)$$

$$W_i^{(2b)}(x) = \frac{-Z_i e}{\epsilon} \int_V d\mathbf{r}' \frac{\rho^{\text{CH}}(x')}{|\mathbf{r} - \mathbf{r}'|}, \quad (3.12)$$

$$W_i^{(3)}(x) = \frac{Z_i e\kappa}{\epsilon} \int_V d\mathbf{r}' \rho^{\text{CH}}(x') \quad (3.13)$$

and

$$\rho^{\text{NUM}}(x) = \sum_i \rho_i [1 + h_i(x)], \quad (3.14)$$

$$\rho^{\text{CH}}(x) = \sum_i \rho_i Z_i e h_i(x) \quad (3.15)$$

are the number and charge densities in the double layer, respectively. There are two types of effects due to finite ion size. The first, and more obvious one, is the hard sphere excluded volume effect. The other is a size effect on the electrostatic interaction. We shall consider their contribution to the potential of mean force between an ion and the surface $W_i(x)$ in detail.

The first term on the right-hand side of Eq. (3.10) is the mean electrostatic potential energy for a *point* ion at x and is the only term in the PB+S expression for $W_i(x)$. The next two terms $W_i^{(2a)}$ and $W_i^{(2b)}$ are of the same order in density. $W_i^{(2a)}$ accounts for pure hard sphere interactions between the ions, and in the HNC/MSA the stress tensor due to such interactions is approximated by $[\rho^{\text{NUM}}(x) kT] \mathbf{I}$. Thus the integral in large parentheses in Eq. (3.11), which is taken over the surface of a sphere of radius R around an ion centered at x , is just the x component of the force exerted on the ion, and $W_i^{(2a)}$ is the work done against this force. Apart from a misprinted factor of $\frac{1}{2}$ this is identical to the Buff and Stillinger excluded volume term.¹⁰ Since the average ionic density in the region 0 to x is larger than that in the region x to ∞ , $W_i^{(2a)}$ is a repulsive contribution to the potential of mean force. It will tend to thicken the double layer and increase the magnitude of the electrostatic potential relative to that predicted by the PB theory.

We now consider the term $W_i^{(2b)}$, Eq. (3.12). Since the first term on the right-hand side of Eq. (3.10), $Z_i e\psi(x)$ is the mean electrostatic energy of a *point* ion located at x , it has also included electrostatic interactions between ion i and all other ions whose centers are within a distance less than R from x . As the ion i has a finite size, these extra interactions must be subtracted from $Z_i e\psi(x)$. $W_i^{(2b)}$ represents this correction because the integral in Eq. (3.12), which is taken over the volume of a sphere of radius R around an ion centered at x , is the *negative* of the electrostatic interaction between an ion at x and all ions within a distance R from x . Since the sign of the diffuse layer charge $\rho^{\text{CH}}(x)$ is opposite to that of the potential $\psi(x)$, the term $W_i^{(2b)}(x)$ is an attractive correction for counter-ions and repulsive for co-ions. The net result is a compression of the double layer in which the counter-ions are present in the majority. Therefore the correction term $W_i^{(2b)}(x)$ will decrease the magnitude of the electrostatic potential relative to that predicted by the PB theory. The term $Z_i e\psi(x) + W_i^{(2b)}(x)$ is identical to the cavity term $Z_i e\psi^{\text{cav}}(x)$ of Buff and Stillinger,¹⁰ that is,

$$Z_i e \psi^{\text{cav}}(x) = Z_i e \psi(x) + W_i^{(2b)}(x) \\ = \frac{1}{2} Z_i e [\psi(x+R) + \psi(x-R)] . \quad (3.16)$$

The term $W_i^{(3)}(x)$ represents a correction on $W_i^{(2b)}(x)$ due to rearrangements of the self-atmosphere of ion i .¹¹ It is clear that its effect is opposite to that of $W_i^{(2b)}(x)$ but is a correction of lower order in density.

While we have only considered the leading terms in the density expansion of the potential of force, the HNC/MSA contains higher order corrections for finite ion size due to pure hard sphere effects (terms such as $W_i^{(2a)}$) as well as finite size corrections to the electrostatics (terms such as $W_i^{(2b)}$, $W_i^{(3)}$). The relative importance of these two effects will be assessed in a numerical solution of the HNC/MSA equations.

It is interesting to observe that the first few terms of the density expansion of the HNC/MSA potential of mean force, Eqs. (3.10)–(3.13), is identical to the exact density expansion based on the potential theory approach.^{1,10,11} At first sight this may seem surprising because at low concentrations the MSA predicts unphysical behavior for the *bulk* pair distribution functions between ions—that is, the bulk pair distribution function between co-ions becomes negative near contact. However, since the MSA exhibits the exact Debye–Hückel limiting law this unphysical behavior near contact has negligible effects on the bulk thermodynamic properties which depend on integrals of the distribution functions. Thus it is suggestive that the HNC/MSA surface charge-surface potential relationship which is also a thermodynamic result dependent on integrals of wall-ion distribution functions, will be quite reasonable at low concentrations in spite of the problems with bulk MSA distribution functions. Using a perturbative scheme, Henderson and Blum¹⁶ found that at $10^{-4} M \psi_\beta$ predicted by the HNC/HNC is considerably lower than the PB result, Eq. (3.9), for surface charge densities $\geq 0.1 \text{ C m}^{-2}$. In the same regime the HNC/MSA result is very close to the PB result.

IV. RESULTS AND DISCUSSION

The HNC/MSA equations [Eqs. (2.22), (2.25), (2.26), and (3.1)–(3.7)] have been solved by a direct iteration method for a 1:1 electrolyte at concentrations 0.01, 0.1, and 0.5 mole dm^{-3} and surface charge density 0–0.8 C m^{-2} . Other solution parameters are $\epsilon = 78.5$, $T = 298 \text{ K}$, and $R = 4.25 \text{ \AA}$. The numerical scheme has also been tested against the Poisson–Boltzmann theory ($e_{ij}^0 = 0$) and the MSA/MSA {replacing $\ln[1 + h_i(x)]$ by $h_i(x)$ in Eq. (3.1)} with agreement to within 1% for all parameter ranges. The contact values condition, Eq. (2.29), is also satisfied to within the same accuracy.

The counter-ion and co-ion correlation functions in the HNC/MSA and the PB+S theory are compared in Fig. 1 for a bulk electrolyte concentration of 0.1 mole dm^{-3} and a surface charge density of 0.16 C m^{-2} . In the vicinity of the charged surface where the local ionic concentration is high, the various correction terms outlined in Eq. (3.10) are expected to be important. For example, the excluded volume $W_i^{(2a)}$ and electrostatic $W_i^{(2b)}$ correc-

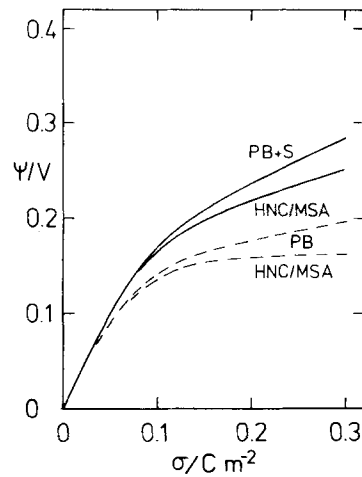


FIG. 2. Potential at the charge surface ψ_0 (—) and at the plane of centers of closest approach of the ions ψ_β (---) as a function of the surface charge density σ , at 0.01 mole cm^{-3} electrolyte concentration. Other parameters are as Fig. 1. Present work (HNC/MSA); Poisson–Boltzmann + Stern layer (PB+S).

tions tend to repel co-ions from the surface and this is reflected in co-ion correlation function being more negative near the surface in the HNC/MSA than in PB+S theory. In the same region, the counter-ions are more strongly adsorbed in the HNC/MSA which indicates that the electrostatic correction is more important in this case. Further away from the surface, the HNC/MSA and PB+S results intersect in order to preserve charge neutrality, cf. Eq. (2.26). Because of this crossover, the ionic adsorption excesses

$$\Gamma_i = \rho_i \int_0^\infty h_i(x) dx \quad (4.1)$$

for the HNC/MSA are practically identical to those of the PB+S theory throughout the range of electrolyte concentrations and surface charge densities that we have studied. The overall picture is that the HNC/MSA density profiles which include finite ion size effects are of shorter range than those of PB+S. This is in agreement with the observation that the effective decay length of the potential or density profile κ_{eff}^{-1} due to using e_{ij}^{MSA} is smaller than the familiar Debye length κ^{-1} .¹²

The implication of this on the surface charge-surface potential relationship is that for the same surface charge the HNC/MSA surface potentials ψ_0 and ψ_β are lower than the PB+S values (Figs. 2–4) because the surface potential is a measure of the degree of charge separation, see Eq. (2.25). We also note that for low to moderate surface charge densities, there is little difference between the HNC/MSA and PB+S theory owing to the mutually canceling effects due to excluded volume and electrostatic corrections. This serendipity has been reported before.¹³ One other interesting feature in Figs. 2–4 is the maximum in ψ_β as a function of surface charge density. Although we are certain that this is not an artifact of the HNC/MSA since it is also observed in the HNC/HNC calculation,² we cannot prove conclusively that this maximum actually occurs in a primitive model double layer. However, we do know that at very high

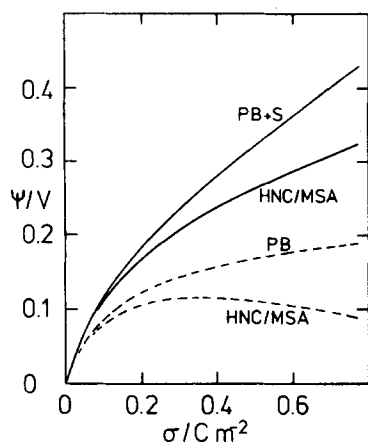


FIG. 3. As for Fig. 2 but at 0.1 mole dm^{-3} electrolyte concentration.

surface charge densities, σ (possibly beyond the range in Figs. 2–4) ψ_β must increase with increasing σ when the ions in the double layer become close packed. We are fairly certain that we are not within this close packed regime because we have checked that for our range of electrolyte concentrations and surface charge densities, the average ionic densities in a slab of thickness R and in a spherical volume of diameter R have not exceeded physical close packed limits. Consequently, the nature of the maximum in ψ_β is a point that should perhaps be investigated by simulation studies.¹⁴

Finally, in Fig. 5 we show the differential diffuse layer capacitance given by

$$C_\beta = \partial\sigma / \partial\psi_\beta \quad (4.2)$$

as a function of surface potential for an electrolyte concentration of 0.5 mole dm^{-3} . The larger values of C_β in the HNC/MSA is again a reflection that for low to moderate surface charges in the diffuse layer is more compact when ion size effects are included.

V. CONCLUSION

For electrolyte concentrations ($\leq 0.1 \text{ mole dm}^{-3}$) and surface charge densities ($\leq 0.2 \text{ C m}^{-2}$) of interest to col-

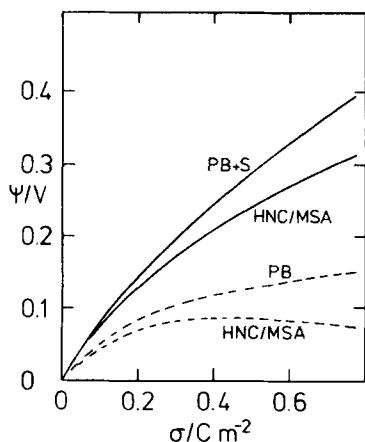


FIG. 4. As for Fig. 2 but at 0.5 mole dm^{-3} electrolyte concentration.

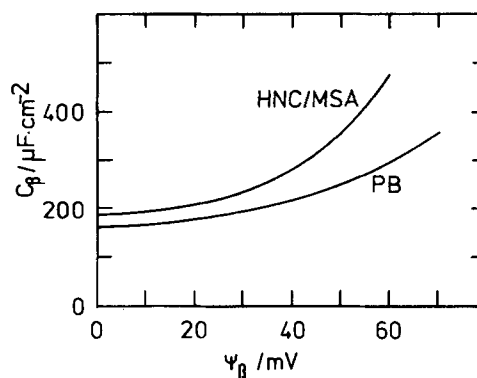


FIG. 5. Capacitance of the diffuse double layer C_β [Eq. (4.2)] as a function of the potential at the plane of centers of closest approach of the ions ψ_β . Electrolyte concentration 0.5 mole dm^{-3} . Other details as in Fig. 1.

loid and surface chemistry, the Poisson–Boltzmann theory with a simple Stern layer correction will give a good description of the primitive model electrolyte at a charged surface.¹⁴ The present integral equation approach indicates that as a function of surface charge density, the potential at the plane of closest approach of the diffuse layer ions exhibits a maximum at high surface charge densities. Although we cannot completely rule out the possibility that this is an artifact of the integral equation method, this is an interesting result that warrants further investigation.

In terms of describing the properties of real electrical double layers, the primitive model still requires extensive modifications, in particular, assumptions about the structure of the Stern region. We have made preliminary studies of the Stern layer using an ion-dipole mixture to model the electrolytes. The results will be published shortly.

ACKNOWLEDGMENT

Since the completion of this work we became aware of a similar calculation by D. Henderson *et al.* who used the HNC/HNC approximation (Ref. 2). We thank D. Henderson for making available preprints of Refs. 2 and 16.

APPENDIX

We derive the expression for the contact values for the surface–fluid distribution function for (a) an electrolyte against a charged wall and (b) a nonelectrolyte fluid mixture at a surface. The wall–fluid direct correlation function is assumed to be given by the HNC closure.

Consider first the electrolyte problem. From Eq. (2.23) the potential of mean force of ionic species i at a distance x from the wall is

$$-\beta W_i(x) = \ln[1 + h_i(x)] = -\beta Z_i e\psi(x) + \sum_j \rho_j \int_{-\infty}^{\infty} dy e_{ij}^0(|x-y|) h_j(y) \quad (A1)$$

The force acting on a slab of fluid confined between the planes $x=0$ and $x=z$ by the fluid in $x \geq z$ is

$$F(z) = - \sum_i \rho_i \int_0^z dx (1 + h_i(x)) \frac{dW_i(x)}{dx}. \quad (\text{A2})$$

Using the first equality in Eq. (A1), the force acting on the fluid on $x \geq 0$ is

$$F(\infty) = kT \sum_i \rho_i \int_0^\infty dx \frac{dh_i(x)}{dx} = -kT \sum_i \rho_i h_i(0). \quad (\text{A3})$$

Another expression for $F(\infty)$ can be derived using the second equality in Eq. (A1) for $W_i(x)$. From the one dimensional Poisson equation and Eq. (2.26) we have the identity

$$\sum_i \rho_i z_i e \int_0^\infty (1 + h_i(x)) \frac{d\psi(x)}{dx} dx = \frac{2\pi\sigma^2}{\epsilon} = \frac{\epsilon E^2}{8\pi}. \quad (\text{A4})$$

Thus, combining Eqs. (A1)–(A4) we have

$$F(\infty) = -kT \sum_i \rho_i h_i(0) = -\frac{\epsilon E^2}{8\pi} + \lim_{z \rightarrow \infty} I(z), \quad (\text{A5})$$

where

$$I(z) = 2\pi kT \sum_{i,j} \rho_i \rho_j \int_{-\infty}^\infty dy \int_0^z dx (1 + h_i(x)) \times (x - y) c_{ij}^0(|x - y|) h_j(y). \quad (\text{A6})$$

Since $I(z)$ only involves short ranged direct correlation functions, the evaluation of this term is the same for cases (a) and (b). To evaluate this we replace $h_i(y)$ by $g_j(y) = 1 + h_j(y)$ since the dy integral is odd about $y = x$. Putting $t = x - y$, we get

$$I(z) = 2\pi kT \sum_{i,j} \rho_i \rho_j \int_0^\infty dt t c_{ij}^0(t) \int_0^z dx g_i(x) \times [g_j(x - t) - g_j(x + t)] \\ = -2\pi kT \sum_{i,j} \rho_i \rho_j \int_0^\infty dt t c_{ij}^0(t) \times \int_{x-t}^x dx [g_i(x) g_j(x + t)], \quad (\text{A7})$$

where the second member of Eq. (A7) follows from $g_i(x) = 0$, $x < 0$ [see Eq. (2.22)]. Now as $z \rightarrow \infty$ and since c_{ij}^0 is a short ranged function, the integrand in brackets may be replaced by unity because $h_i(x) \rightarrow 0$ as $x \rightarrow \infty$. Thus from Eq. (A5) we have the result

$$kT \sum_i \rho_i h_i(0) = \frac{\epsilon E^2}{8\pi} - \frac{1}{2} kT \sum_{i,j} \rho_i \rho_j \bar{c}_{ij}^0(0), \quad (\text{A8})$$

where $\bar{c}_{ij}^0(k)$ is the three dimensional Fourier transform of $c_{ij}^0(r)$. From the Kirkwood–Buff theory,¹⁵ the compressibility of a fluid mixture is

$$\chi = kT \left(\sum_i \rho_i - \sum_{i,j} \rho_i \rho_j \bar{c}_{ij}^0(0) \right)^{-1}. \quad (\text{A9})$$

For an electrolyte, we have

$$\sum_{i,j} \rho_i \rho_j \bar{c}_{ij}^0(0) = \sum_{i,j} \rho_i \rho_j \bar{c}_{ij}^0(0),$$

because of the bulk electroneutrality condition [see Eqs. (2.17) and (2.18)]. Combining Eqs. (A8) and (A9) we have the desired result, Eq. (2.28),

$$kT \sum_i \rho_i (1 + h_i(0)) = \frac{\epsilon E^2}{8\pi} + \frac{1}{2} \left(kT \sum_i \rho_i + \chi^{-1} \right). \quad (\text{A10})$$

For the case of a simple fluid (nonelectrolyte) at a surface where the surface-fluid potential consists of a hard core part plus a tail $\phi_i(x)$, $\beta Z_i e \psi(x)$ in Eq. (A1) is replaced by $\beta \phi_i(x)$ in the HNC approximation, and the result for the contact value is

$$kT \sum_i \rho_i (1 + h_i(0)) = \sum_i \rho_i \int_0^\infty (1 + h_i(x)) \frac{d\phi_i(x)}{dx} dx + \frac{1}{2} \left(kT \sum_i \rho_i + \chi^{-1} \right). \quad (\text{A11})$$

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