A Further Treatment of the Exclusion-volume Term in the Modified Poisson–Boltzmann Theory of the Electric Double Layer

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The first equation of the Born–Green–Yvon hierarchy of distribution functions is used to calculate the exclusion-volume term in the modified Poisson–Boltzmann theory. Comparisons with Monte-Carlo calculations indicate that this theory is an improvement upon the modified Poisson–Boltzmann theory based on a bulk density expansion of the exclusion-volume term, especially at the higher values of the surface charge and electrolyte concentration. Some imaging results for a metallic and insulating wall are also presented.

INTRODUCTION

The most widely used and perhaps the most successful theory of the electric double layer is that of Gouy,[1] Chapman[2] and Stern[3] (GCS). Monte-Carlo (MC) calculations of Torrie and Valleau[4] and van Megen and Snook[5] for a 1 : 1 restricted primitive model electrolyte in the neighbourhood of a plane charged wall without imaging have verified the accuracy of the GCS theory at low values of the surface charge and electrolyte concentration. Various alternatives to the GCS theory have been recently developed from the integral equation treatments of the homogenous bulk electrolyte phase. The mean spherical approximation (MSA) has been studied by Blum,[6] Henderson and Blum,[7] Levine and Outhwaite[8] and Outhwaite, Bhuiyan and Levine;[9] extensions of the MSA by Henderson and Blum[10] and Henderson, Blum, McQuarrie and Olivares;[11] the hypernetted chain equation by Henderson, Blum and Smith;[12] the hypernetted chain equation with the bulk MSA direct correlation function by Carnie, Chan, Mitchell and Ninham.[13] Also an application of the Born–Green–Yvon (BGY) integral equation has been made by Croxton and McQuarrie.[14] In one aspect or another these new theories have an advantage over the classical GCS theory but none of them has proved to be outstandingly success-ful.[15] Furthermore, apart from an extension of the BGY theory[14] none of the new theories is yet able to cope with imaging effects.

We consider here an extension of the so-called modified Poisson–Boltzmann (MPB) theory of the electric double layer. The MPB theory is a development of the mean electrostatic potential approach initiated by Gouy and Chapman which is based on the classical statistical analysis of Kirkwood[16] and Loeb's closure.[17] Details of the development of the theory can be found in ref. (8). The MPB equation (specifically the MPB4 equation) has been found to reproduce the MC

results more accurately than the GCS theory and it also treats imaging.[18] Unfortunately the numerical solution of the MPB4 equation fails at high values of the surface charge and the accuracy of the solution, compared with the MC calculations, diminishes at the higher values of the surface charge and electrolyte concentration. To extend the range of the MPB4 equation we treat here a reformulation of the exclusion-volume term within the BGY framework. The ensuing MPB equation is found to be an improvement over the MPB4 equation.

THEORY

Poisson's equation is the fundamental equation governing the mean electrostatic potential $\psi(1)$ at any point r_1 in the diffuse layer. For a restricted primitive model electrolyte in the neighbourhood of a uniformly charged plane wall Poisson's equation is

$$\frac{d^2\psi}{dx_1^2} = -(4\pi/\varepsilon) \sum_s e_s n_s^0 g_{0s}(x_1) \tag{1}$$

where e_s is the charge on an ion of species s, n_s^0 is the bulk number density of ions of species s, x_1 is the perpendicular distance from the wall into the electrolyte, ε is the bulk dielectric constant and $g_{0s}(x_1)$ is the wall–ion distribution function.

To utilise eqn (1) it is necessary to represent $g_{0s}(x_1)$ in terms of $\psi(x_1)$. This is an intractable problem and recourse has to be made to various approximation schemes. We consider here the MPB theory which is based on the Güntelberg charging process and Loeb's closure. An alternative potential theory[19] which is more complex is based on the BGY hierarchy. Within the MPB theory it has been shown that

$$g_{0s}(x_1) = \zeta_s(x_1) \exp \left\{ -\tfrac{1}{2}\beta e_s \left[(e_s/\varepsilon a)(F - F_0) + F\psi(x_1 + a) + F\psi(x_1 - a) \right. \right.$$
$$\left. \left. - \frac{(F-1)}{a} \int_{x_1-a}^{x_1+a} \psi(X)\, dX \right] \right\} \tag{2}$$

where $\zeta_s(x_1) = g_{0s}(x_1|e_s = 0)$ is the exclusion-volume term, $\beta = 1/kT$, a is the ionic diameter and

$$F = (1 + f\delta_2)/[(1 + \kappa a)(1 - f\delta_1)], \qquad x \geq a \tag{2a}$$

$$\delta_2 = \exp[\kappa(a - 2x)] \sinh(\kappa a)/(2\kappa x) \tag{2b}$$

$$\delta_1 = \delta_2[\kappa a \cosh(\kappa a) - \sinh(\kappa a)]/[(1 + \kappa a)\sinh(\kappa a)] \tag{2c}$$

$$F = \left\{ 2(1 + \kappa x)\exp(-\kappa a) + 2(1 - \kappa a)\exp(-\kappa x) + 2\kappa^2 ax \int_x^a r^{-1}\exp(-\kappa r)\, dr \right.$$
$$\left. + (f/\kappa x)[\exp(-\kappa a) + 2\kappa(a - x)\exp(-\kappa x) - \exp(-\kappa(2x + a))] \right\}$$
$$\Big/ \{2[\exp(-\kappa a)(1 + \kappa(x + a)) + \exp(-\kappa x)] - (f/\kappa x)[2\kappa x \exp(-\kappa x)$$
$$+ (1 + \kappa a)(\exp(-2\kappa x) - 1)\exp(-\kappa a)]\}, \qquad \frac{a}{2} \leq x \leq a \tag{2d}$$

$$\kappa^2 = (4\pi\beta/\varepsilon) \sum_s e_s^2 n_s^0 g_{0s}(x_1) \tag{2e}$$

$$F_0 = \lim_{x \to \infty} F = (1 + \kappa_0 a)^{-1}, \qquad \kappa_0 = \lim_{x \to \infty} \kappa. \tag{2f}$$

See ref. (18) for further details.

Previously the exclusion-volume term has been treated in the first-order bulk density expansion of Levine and Bell[20]

$$\zeta_s(x_1) = H\left(x_1 - \frac{a}{2}\right)\left\{1 + (4\pi a^3/3)\sum_t n_t^0 \right.$$
$$\left. + \pi \sum_t n_t^0 \int_{\max(a/2,\,x_1-a)}^{x_1+a} [(X-x_1)^2 - a^2]g_{0t}(X)\,\mathrm{d}X\right\} \quad (3)$$

where $H(x_1)$ is the Heaviside (unit step) function and the wall is at $x_1 = 0$. When eqn (1) is used in conjunction with eqn (2) and (3) the system is called the MPB4 equation.[18] Computations with the MPB4 equation indicated that a better approximation to $\zeta_s(x_1)$ was required to extend the MPB equation to higher values of the surface charge and electrolyte concentration.

A logical calculation of $\zeta_s(x_1)$ within the Güntelberg framework is to consider charging up the wall (see, for example, Carnie, Chan, Mitchell and Ninham[13]). Taking the interaction energy of an ion t at r_2 with the wall at a stage λ in the charging process to be $e_t \lambda \psi_m(2)$, where $\psi_m(2)$ is the potential due to the surface charge density, then

$$\zeta_s(x_1) = g_{0s}^0(x_1) \exp\left\{-\beta \int_0^1 \int \sum_t e_t n_t^0 \psi_m(2) g_{0t}(2|\lambda)[g_{st}(1,2|\lambda|e_s=0)-1]\,\mathrm{d}2\,\mathrm{d}\lambda\right\} \quad (4)$$

where $g_{0s}^0(x_1)$ is the uncharged-ion–uncharged-wall distribution function in a sea of fully charged ions and $g_{st}(1,2|\lambda)$ is the pair distribution function for ions s and t in the neighbourhood of the wall at a stage λ in the charging process. To a good approximation $g_{0s}^0(x_1)$ could be approximated by the Percus–Yevick value for uncharged systems with $g_{st}(1,2|\lambda|e_s=0)$ approximated by Loeb's closure. Unfortunately the difficulty in implementing the charging integration does not make this method of calculating $\zeta_s(x_1)$ very attractive.

A derivation of eqn (3) from eqn (4) can be seen by following the analysis of Carnie, Chan, Mitchell and Ninham.[13] Introducing the non-uniform direct correlation function $c_{st}(1,2)$ defined through the non-uniform Ornstein–Zernike equation, eqn (4) can be transformed to

$$\zeta_s(x_1) = g_{0s}^0(x_1) \exp\left[-\beta \int_0^1 \int \sum_t n_t^0 c_{st}(1,2|\lambda|e_s=0)\frac{\partial}{\partial\lambda}g_{0t}(2|\lambda)\,\mathrm{d}2\,\mathrm{d}\lambda\right]. \quad (5)$$

This equation is implicit in the work of Saam and Ebner.[21] Since $e_s = 0$ we expect $c_{st}(1,2|\lambda|e_s=0)$ to be a short-ranged function, so to a good approximation we may replace it by the uncharged bulk correlation function $c_{st}^0(r_{12})$. In this case eqn (5) reduces to

$$\zeta_s(x_1) = g_{0s}^0(x_1) \exp\left\{-\beta \int \sum_t n_t^0 c_{st}^0(r_{12})[g_{0t}(2)-1]\,\mathrm{d}2\right\}. \quad (6)$$

The first-order density expansion (3) of Levine and Bell follows directly from eqn (6) on linearising and putting

$$g_{0s}^0(x_1) = H(x_1 - a/2)$$

and

$$c_{st}^0(r_{12}) = -H(a - r_{12}).$$

Replacing $g_{0s}^0(x_1)$, $c_{st}^0(r_{12})$ by the corresponding Percus–Yevick or other known approximate values gives a possible mechanism for improving upon the calculation of the exclusion-volume term.

The basic difficulty with the charging process is the unknown dependence of the distribution and correlation functions upon the charging parameter λ. To avoid this particular problem we now consider the first equation of the BGY hierarchy of distribution functions. The first equation gives

$$\zeta_s(x_1) = \exp\left\{-\left[u_s(x_1) + \int_\infty^{x_1} \sum_t \int \hat{\boldsymbol{x}} \cdot \nabla_1 u_{st}(r_{12}) n_t^0 g_{0t}(2) g(1,2|e_s=0)\, d2\, dx\right]\right\} \quad (7)$$

where $u_s(x_1)$ is the short-range non-electrostatic interaction of the ion s with the wall and $u_{st}(r_{12})$ is the short-range non-electrostatic ion–ion pair interaction. For our model

$$u_s(x_1) = \begin{cases} 0, & x_1 > a/2 \\ \infty, & x_1 < a/2 \end{cases} \quad (8)$$

$$\beta \nabla_1 u_{st}(r_{12}) \exp\left[-\beta u_{st}(r_{12})\right] = -\delta(r_{12}-a)\hat{\boldsymbol{r}}_{21}. \quad (9)$$

So introducing eqn (8) and (9) into eqn (7) and using the delta function properties

$$\zeta_s(x_1) = H\left(x_1 - \frac{a}{2}\right)\exp\left[-\int_\infty^{x_1} \sum_t n_t^0 \int_{S_{12}} \hat{\boldsymbol{x}} \cdot \hat{\boldsymbol{r}}_{12} g_{0t}(2) g_{st}(1,2|e_s=0)\, dS_2\, dx\right] \quad (10)$$

where S_{12} is the surface of the sphere $r_{12} = a$.

Now we have exactly that[22,23]

$$g_{st}(1,2|e_s=0) = \zeta_{st}(1,2)\exp\left\{-\beta e_t\left[\phi(1;2|e_s=0) + \int_0^1 \lim_{3\to2} \phi(1,2;3|e_s=0)\, d\lambda\right]\right\} \quad (11)$$

where $\phi(1;2)$, $\phi(1,2;3)$ are fluctuation potentials for one and two fixed ions, respectively, $\zeta_{st}(1,2) = g_{st}(1,2|e_s=e_t=0)$ and λ is the charging parameter associated with e_t at r_2. Note that Féat and Levine[22] state that $\phi(1;2|e_s=0)=0$, which is untrue in general. Loeb's closure for $g_{st}(1,2|e_s=0)$ follows on putting $\zeta_{st}(1,2) = H(r_{12}-a)$ and $\phi(1,2;3|e_s=0)=0$. Neglecting the fluctuation potential $\phi(1,2;3|e_s=0)$ in eqn (11) and substituting for $g_{st}(1,2|e_s=0)$ in eqn (10)

$$\zeta_s(x_1) = H\left(x_1 - \frac{a}{2}\right)\exp\left(-2\pi\int_\infty^{x_1} \sum_t n_t^0 \int_{\max(a/2,\,x-a)}^{(x+a)}\right.$$
$$\left. \times (X-x)\zeta_{st}(a)g_{0t}(X)\exp\left[-\beta e_t\Phi(x,X)\right]\, dX\, dx\right) \quad (12)$$

where $\Phi(x,X) = \phi(1;2|e_s=0|r_{12}=a)$ and $\zeta_{st}(a) = \zeta_{st}(1,2|r_{12}=a)$. The exclusion-volume term used in the MPB4 equation is recovered from eqn (12) by putting $\zeta_{st}(a)=1$ and $\Phi(x,X) \simeq 0$, interchanging the order of integration, integrating with respect to x and then expanding to first order in bulk densities. Eqn (12) thus gives a technique for estimating the exclusion-volume term solely within Loeb's closure and the BGY hierarchy.

RESULTS AND DISCUSSION

We now consider the implications of solving the Poisson equation, eqn (1), with $g_{0s}(x_1)$ given by eqn (2) and the BGY exclusion-volume term, eqn (12). In the

BGY $\zeta_s(x_1)$ we take $\zeta_{st}(a) = 1$ and calculate $\Phi(x, X)$ in a manner similar to the derivation of eqn (2) (see Appendix). This new MPB equation we will simply call the MPB equation. To facilitate the numerical evaluation of the exclusion-volume term we rewrite eqn (12) as

$$\zeta_s(x_1) = H\left(x_1 - \frac{a}{2}\right) \exp\left\{-2\pi \int_\infty^{x_1} \sum_t n_t^0 \int_{\max(a/2, x-a)}^{(x+a)} (X - x)\right.$$
$$\times [g_{0t}(X) \exp(-\beta e_t \Phi(x, X)) - 1] \, dX \, dx$$
$$+ (\pi/3) H\left(\frac{3a}{2} - x_1\right)\left(\frac{3a}{2} - x_1\right)^2 \left(x_1 + \frac{3a}{2}\right) \sum_t n_t^0 \right\} \tag{13}$$

where the extra term added to the integrand (which integrates out to zero for $x_1 > 3a/2$) improves the convergence of the integral for large x. Numerical solutions of the MPB equation were found by the quasi-linearisation technique used in solving the MPB4 equation.[18] The calculations were performed for $1:1$ electrolytes at the MC parameters of Torrie and Valleau,[4] the electrolyte parameters being $a = 4.25$ Å, $\varepsilon = 78.5$ and $T = 298$ K. Other MC calculations have been made by van Megen and Snook,[5] these authors being primarily concerned with a discrete surface charge distribution. MPB results are also presented for a metallic wall ($f = -1$) and an insulating wall ($f = 0.9748$). Here f is the electrostatic imaging factor given by $f = (\varepsilon - \varepsilon_w)/(\varepsilon + \varepsilon_w)$, where ε_w is the dielectric constant of the wall.

We consider first the case of no imaging ($f = 0$). Fig. 1 shows the variation of the diffuse layer potential drop with surface charge at $c = 0.01, 0.1$ and 1 mol dm^{-3}.
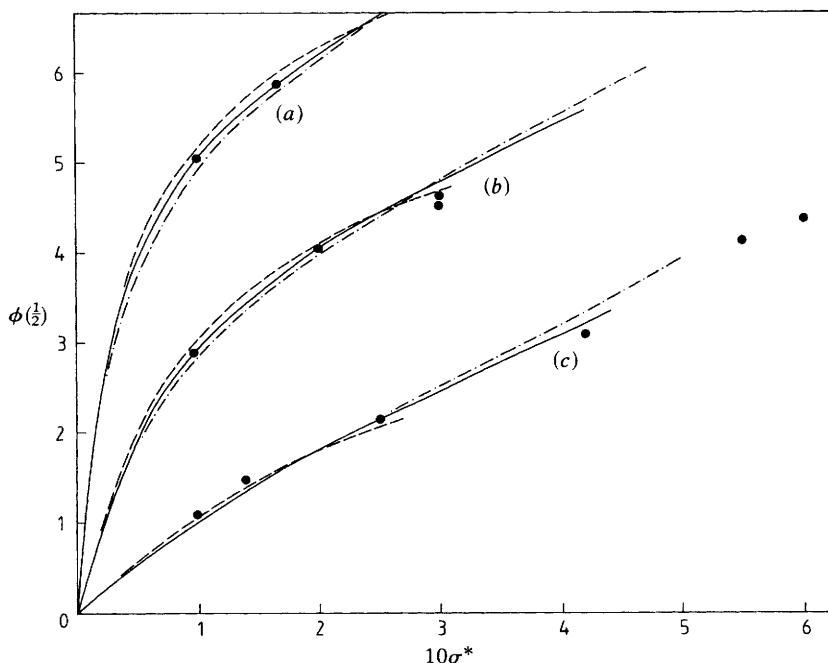

FIG. 1.—Variation of the diffuse layer potential drop $\phi(\frac{1}{2})$($\phi = |e|\beta\psi$) with surface charge σ^* ($\sigma^* = \sigma a^2/|e|$) at the three concentrations $c = (a)$ 0.01, (b) 0.1 and (c) 1 mol dm^{-3}. The curves marked (———), (—·—·—) and (– – – –) are for no imaging, a metallic wall and an insulating wall, respectively. The solid points are the MC points of Torrie and Valleau[4] for no imaging.
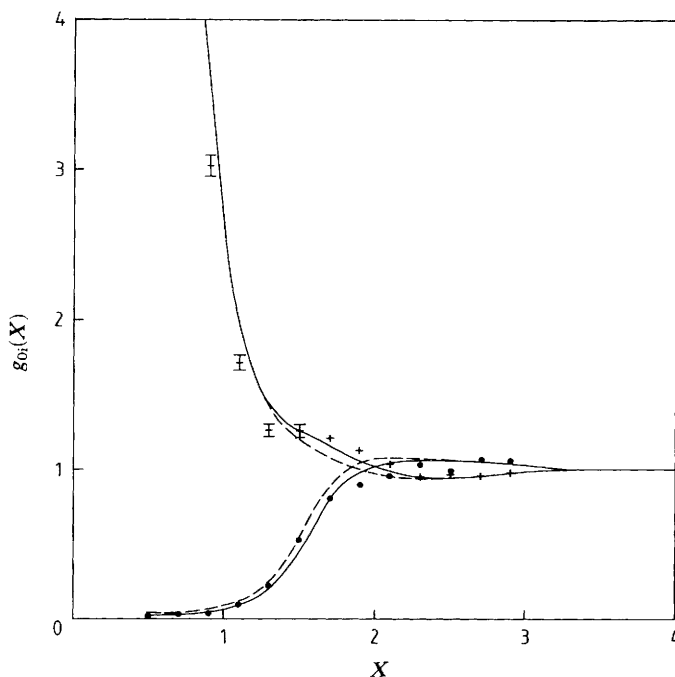
FIG. 2.—Co-ion and counter-ion profiles $g_{0i}(X)$ ($X = x/a$) at $c = 1.9676$ mol dm^{-3}, $\sigma^* = 0.396$ for no imaging with the MC points ($\bullet$, +) of Torrie and Valleau.[4] (‑ ‑ ‑) denotes MPB4 curve.[18]

There is good agreement between the MPB and MC results, especially at $c = 0.01$ mol dm^{-3} and for $c = 0.1$ mol dm^{-3} at the lower values of the surface charge. The MPB and MPB4 equations give similar predictions at the two lower concentrations but the MPB equation is in better agreement with the MC results at $c = 1$ mol dm^{-3}. Furthermore, the MPB equation can be solved for higher values of the surface charge than the MPB4 equation. In fig. 2 and 3 the singlet ion distribution function $g_{0i}(x)$ and the mean electrostatic potential $\psi(x)$ are compared with the MPB4 and MC results at $c = 1.9676$ mol dm^{-3} with reduced surface charge $\sigma^* = 0.396$. Again the MPB equation is in closer agreement with the MC results. The MPB $g_{0i}(x)$ accurately predict the damped oscillatory feature of the MC calculations and also agree closely with the MC values in the neighbourhood of the wall, especially the co-ion $g_{0i}(x)$. The only feature not seen in the MPB $g_{0i}(x)$ is the shoulder in the MC counter-ion profile near $x = 1.5a$ due to the packing of counter-ions at the surface. Only the possible suggestion of an "echo" of this effect can be seen in the MPB counter-ion $g_{0i}(x)$. The inability of the MPB theory to treat this packing effect accurately is reflected in the computed mean electrostatic potential, fig. 3, which overestimates the potential well. The layering of counter-ions at the wall is clearly demonstrated in the MC calculations[4] at $c = 1$ mol dm^{-3} with $\sigma^* = 0.7$. Unfortunately no solutions of the MPB equation have been found at this combination of electrolyte concentration and surface charge.

In fig. 1 is also displayed the effect of imaging on the variation of the diffuse layer potential drop with surface charge. At low values of the surface charge we get the expected situation that for a fixed surface charge the metallic wall potential
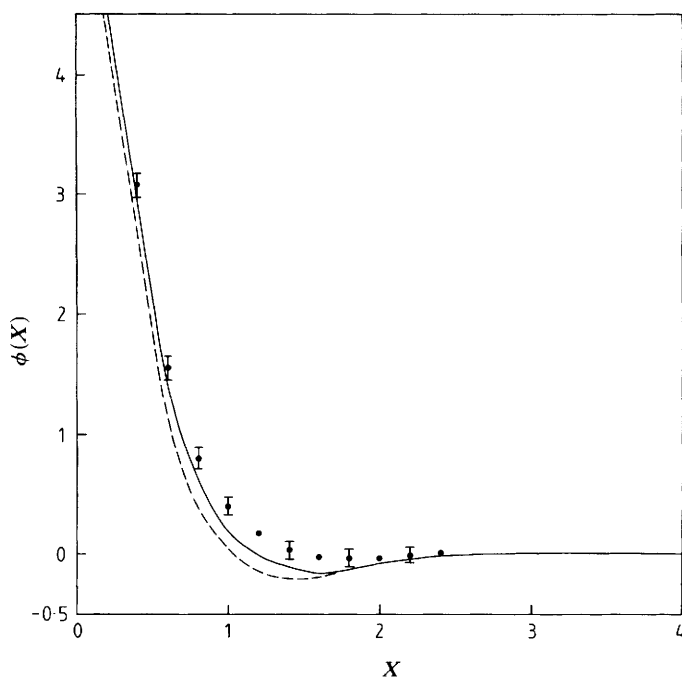
FIG. 3.—Mean electrostatic potential $\phi(X)$ ($\phi = |e|\beta\psi$, $X = x/a$) at $c = 1.9676$ mol dm^{-3}, $\sigma^* = 0.396$ for no imaging with the MC points of Torrie and Valleau.[4] (– – – –) denotes MPB4 curve.[18]

drop is lower and the insulating wall potential drop higher than the no-imaging situation. The reason is simply the increased attractive or repulsive forces experienced by the ions in the neighbourhood of the metallic or insulating wall, respectively. In fig. 4 the singlet ion distribution functions are given at $c = 0.1$ mol dm^{-3}, $\sigma^* = 0.014$ where the influence of the image forces near the wall are displayed, in particular

$$g_{0i}\left(\frac{a}{2}, f = -1\right) > g_{0i}\left(\frac{a}{2}, f = 0\right) > g_{0i}\left(\frac{a}{2}, f = 0.9748\right).$$

The MPB and MC results are in very close agreement.[24] The influence of imaging, especially for a metallic wall, is reduced at $c = 1$ mol dm^{-3} owing to ion shielding. At the higher values of the surface charge we get the surprising result that the deviation of $\psi(a/2)$ from $f = 0$ for the two imaging cases is in the opposite direction to that for low surface charge. This changeover is reflected in the contact values of the counter-ion distribution functions where now

$$g_{0i}\left(\frac{a}{2}, f = -1\right) < g_{0i}\left(\frac{a}{2}, f = 0\right) < g_{0i}\left(\frac{a}{2}, f = 0.9748\right).$$

A similar result is observed in the MPB4 equation. The physical reason for this change is unclear. It could well be some form of counter-ion saturation effect at the surface which for increasing surface charge first occurs for a metallic wall. Numerically the change arises in the mean electrostatic term in eqn (2) swamping the self-image term because of the different values of F. At $c = 0.1$ mol dm^{-3},
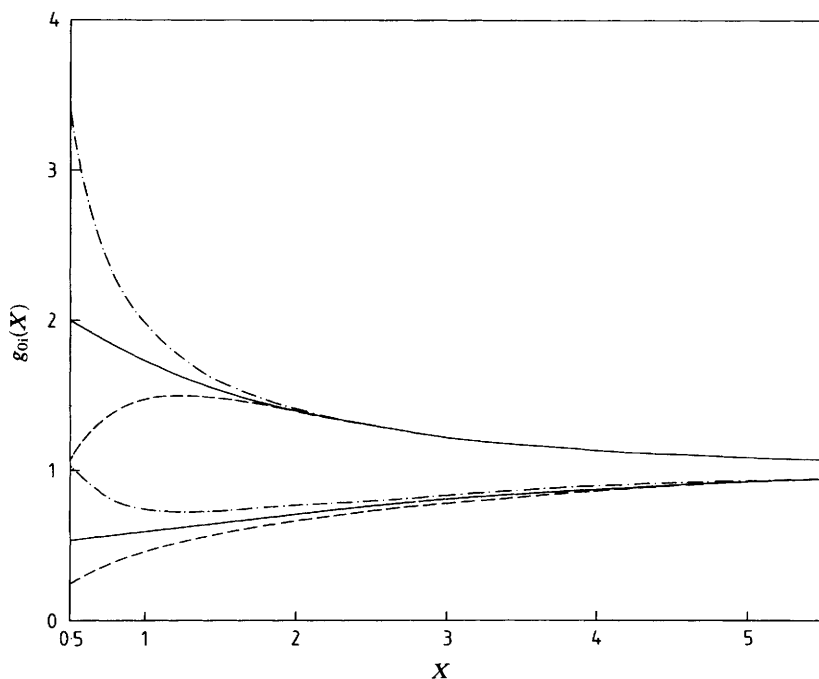
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FIG. 4.—Co-ion and counter-ion profiles at $c = 0.1\,\mathrm{mol\,dm^{-3}}$, $\sigma^* = 0.014$. The curves denoted by (———), (—·—·—) and (— — — —) are for no imaging, a metallic wall and an insulating wall, respectively.

$\sigma^* = 0.3$ we have $F(a/2) = -0.372$, 0.0007 and 1.06 for $f = -1$, 0 and 0.9748, respectively. Further independent work is required to see if this changeover is an artefact of the MPB equation. Incidently the presence of a metallic wall increases the range of σ^* for which a solution can be found and an insulating wall decreases the range.

Various exact conditions exist for the distribution functions and the mean electrostatic potentials. The most well known is the overall neutrality of the surface and diffuse layer charge and we have found that this condition is satisfied to within a few percent by the MPB equation. Henderson, Blum and Lebowitz[25] have derived for no imaging the contact condition

$$kT \sum_s n_s^0 g_{0s}(a/2) = p + (\varepsilon/8\pi)\psi'^2(0) \tag{14}$$

where p is the bulk electrolyte pressure. The MPB equation satisfies this condition fairly well (see the table 1). Note that the BGY equation exactly satisfies this condition.[26] However, even for no surface charge the MPB equation does not satisfy eqn (14) as the evaluation of the exclusion-volume term depends on Loeb's closure. The extension of eqn (14) to cater for imaging has recently been derived by Carnie and Chan.[27] Two further conditions exist, namely the non-uniform analogue of the bulk neutrality condition (the zeroth-moment condition) for a single ion

$$\sum_t e_t n_t^0 \int g_{0t}(2)[g_{st}(1,2) - 1]\,\mathrm{d}2 = -e_s \tag{15}$$

TABLE 1.—CONTACT CONDITION EQN(14) FOR VARIOUS SURFACE POTENTIALS AT $c = 0.01, 0.1$ AND 1 mol dm^{-3}

	$c = 0.01$ mol dm^{-3}		$c = 0.1$ mol dm^{-3}		$c = 1$ mol dm^{-3}	
$\phi(0)$	LHS	RHS	LHS	RHS	LHS	RHS
0	1.00	0.969	1.03	0.945	1.27	1.09
2	3.54	3.34	3.05	2.74	2.43	2.16
4	23.3	21.1	14.2	12.7	6.05	5.90
6	121	109	45.6	43.3	11.7	13.0
8	413	389	100	106	18.2	23.3
10	944	981	167	202		

LHS and RHS denote the left-hand side and right-hand side of eqn (14), respectively, with p calculated from the bulk MPB4 equation (D. M. Burley, V. C. L. Hutson and C. W. Outhwaite, *Mol. Phys.*, 1974, **27**, 225).

and the non-uniform analogue of the second-moment condition of Stillinger and Lovett[28,29]

$$\beta \sum_s e_s n_s^0 \int g_{0s}(1) \phi(1;2) \, d1 = 1. \tag{16}$$

The identity eqn (15) follows directly from Gauss's theorem for the fixed ion at r_1, namely

$$\int_S \frac{\partial \phi}{\partial n}(1;2) \, dS + \int_V \nabla^2 \psi(2) \, d2 = -4\pi e_s / \varepsilon \tag{17}$$

where S is the surface and V the volume of the sphere $r_{12} = a$ centred at r_1 with n the unit outward normal. If $x_1 < 3a/2$ then S is the surface and V the volume of the truncated sphere whose plane face is the exclusion plane $x = a/2$. Eqn (17) is used in the calculation of the fluctuation potential[18,30] and hence the MPB satisfies this condition. The numerical evaluation of eqn (15) and (16) and the contact condition with imaging have not yet been checked numerically as they are awkward to apply. However, we note that as in the bulk theory[29] the normalisation condition eqn (16) is satisfied in the point-ion limit in the MPB theory. This is readily seen as the linear equation governing the fluctuation potential in this case is[30]

$$\nabla^2 \phi(1;2) = (4\pi\beta/\varepsilon)[\sum_t e_t^2 n_t^0 g_{0t}(1)]\phi(1;2) - (4\pi e_s/\varepsilon)\delta(1-2) \tag{18}$$

with the approximate solution[18,30] satisfying $e_t\phi(1;2) = e_s\phi(2;1)$. Using these two results the identity is satisfied on applying the divergence theorem and transforming the wall contribution into $x < 0$.

The numerical results indicate that the new MPB equation using the BGY representation of $\zeta_s(x)$ is an improvement upon the MPB4 equation at the higher values of the electrolyte concentration and surface charge. This is not surprising as $\zeta_s(x)$ in the MPB4 equation is based on a bulk density expansion. For a particular electrolyte concentration the MPB equation can be solved for higher values of the surface charge than the MPB4 equation but unfortunately this extended range of values was not as great as expected. (See fig. 1, where for $f = 0$ no solutions have been found for $\sigma^* \gtrsim 0.43$ at $c = 0.1$ mol dm^{-3} and $\sigma^* \gtrsim 0.45$ at $c = 1$ mol dm^{-3}).

Thus the packing phenomena of the counter-ions at high surface charge predicted by the MC calculations cannot be investigated. To improve the MPB equation requires either (a) a better treatment of the fluctuation potential problem within Loeb's closure or (b) an improvement upon Loeb's closure. The improvement (a) requires a treatment of the non-linear problem for $\phi(1; 2)$, which is extremely difficult. The alternative (b) seems more important and feasible. Possible straight-forward extensions[22,23] to Loeb's closure could be based on

$$g_{st}(1, 2) = \zeta_{st}(1, 2) \exp\left[-\beta e_t \phi(1; 2)\right] \tag{19}$$

or the symmetrical form

$$g_{st}(1, 2) = \zeta_{st}(1, 2) \exp\left\{-\frac{\beta}{2}[e_t\phi(1; 2) + e_s\phi(2; 1)]\right\} \tag{20}$$

with $\zeta_{st}(1, 2)$ being approximated by, for example, the Percus–Yevick uncharged hard-sphere bulk radial distribution function. Such closures would enhance the treatment of excluded-volume effects between two ions which is lacking in Loeb's closure. A higher-order symmetrical closure has been suggested by Féat and Levine[22] but its application is unclear. Without using any improved closure we could have apparently improved our results by replacing $\zeta_{st}(a)$ in the exclusion-volume term, eqn (12), by the Percus–Yevick uncharged hard-sphere contact value. This approximation was tried but no real improvements were found and since it is logically inconsistent within Loeb's closure we have not presented any results.

We now feel that the MPB equation accurately represents the restricted primitive model electrolyte in the vicinity of a plane charged wall for low to moderate values of the electrolyte concentration and surface charge. The MPB equation may not exactly satisfy the contact condition eqn (14), and perhaps the normalisation condition, but the consequence of this appears to be slight when compared with the successful reproduction of many of the MC computations. It thus appears promising to use extensions of the MPB potential approach to treat more complex models of the electric double layer.

APPENDIX

To calculate $\Phi(x, X)[= \phi(1; 2|e_s = 0|r_{12} = a)]$ we use the techniques developed elsewhere.[18,30] For $r_{12} < a$, $x_1 > a/2$ we have the exact equation

$$\nabla^2[\phi(1; 2|e_s = 0) + \psi(x_2)] = 0 \tag{A1}$$

and for $r_{12} \geq a$, $x_1 > a/2$ the approximate solution

$$\phi(1; 2|e_s = 0) = B_0[(1/r_{12}) \exp(-\kappa r_{12}) + (f/r_{12}^*) \exp(-\kappa r_{12}^*)] \tag{A2}$$

where B_0 is independent of r_2, $r_{12}^* = (r_{12}^2 + 4x_1x_2)^{1/2}$ and κ is the local Debye–Hückel parameter defined by

$$\kappa^2 = (4\pi\beta/\varepsilon) \sum_s e_s^2 n_s^0 g_{0s}(x_1). \tag{A3}$$

From eqn (A2) we have that $\Phi(x, X)$ is known provided B_0 can be evaluated at $r_{12} = a$. Now from eqn (A1) we have exactly that

$$\int_S \frac{\partial\phi}{\partial n}(e_s = 0)\,dS = \int_V \nabla^2\psi\,dV \tag{A4}$$

where S and V are defined after eqn (17). So from eqn (A2) and (A4) we have that $B_0(x_1)[= B_0(r_{12} = a)]$ is given by

$$B_0(x_1) = \{\exp(\kappa a)/[4\pi(1 + \kappa a)(1 - f\delta_1)]\}\int_V \nabla^2\psi \, dV, \qquad x_1 \geqslant a \qquad (A5)$$

$$B_0(x_1) = \frac{1}{\pi}\int_V \nabla^2\psi \, dV/\{2[(1 + \kappa x_1 + \kappa a)\exp(-\kappa a) + \exp(-\kappa x_1)]$$

$$-(f/\kappa x_1)[2\kappa x_1\exp(-\kappa x_1) + (1 + \kappa a)\exp(-\kappa a)(\exp(-2\kappa x_1) - 1)]\},$$

$$a/2 \leqslant x_1 \leqslant a \qquad (A6)$$

where

$$\int_V \nabla^2\psi \, dV = 2\pi a\left[\psi(x_1 + a) + \psi(x_1 - a) - (1/a)\int_{x_1-a}^{x_1+a}\psi(y)\,dy\right], \qquad x_1 \geqslant 3a/2 \qquad (A7)$$

$$\int_V \nabla^2\psi \, dV = \pi\left[(2x_1 - a)\psi\left(\frac{a}{2}\right) + \left(x_1 + \frac{a}{2}\right)\left(x_1 - \frac{3a}{2}\right)\psi'\left(\frac{a}{2}\right) + 2a\psi(x_1 + a)\right.$$

$$\left. -2\int_{a/2}^{x_1+a}\psi(y)\,dy\right], \qquad a/2 \leqslant x_1 \leqslant 3a/2 \qquad (A8)$$

and

$$\delta_1 = (\kappa a \cosh \kappa a - \sinh \kappa a)\{\exp[\kappa(a - 2x_1)]\sinh \kappa a\}/[2\kappa x_1(1 + \kappa a)\sinh \kappa a]. \qquad (A9)$$

Hence

$$\Phi(x, X) = B_0(x)\{\exp(-\kappa a)/a + [f/(a^2 + 4xX)^{1/2}]\exp[-\kappa(a^2 + 4xX)^{1/2}]\} \qquad (A10)$$

with $B_0(x)$ given above.

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