

# Approximate Analytic Solution of the Poisson–Boltzmann Equation for a Spherical Colloidal Particle

BY LEE R. WHITE†

School of Chemistry, Bristol University, Cantock's Close, Bristol BS8 1TS

*Received 11th February, 1976*

A novel perturbation scheme is developed to solve the Poisson–Boltzmann equation for the potential profile around a spherical colloidal particle of radius  $a$  in  $z$ - $z$  electrolyte, suitable for values of  $\kappa a$  in the intermediate regime  $1 < \kappa a < 15$ , where the Debye–Hückel linearized solution or the planar solution are not good approximations. The zero'th order solution is shown to be a better approximation to the exact numerical solution than the Debye–Hückel solution for  $\kappa a > 1$  for all values of the surface potential. The first order solution is also exhibited and the range of validity of the approximate solution extended into the small  $\kappa a$  regime. The surface charge and Helmholtz free energy per unit area as functions of  $\kappa a$  and surface potential are also derived and compared with the exact numerical results. The method developed herein is a general one capable of application to the case of unsymmetrical electrolytes and other geometries. As an example of this generality, the zero'th and first order solutions for the Poisson–Boltzmann equation in cylindrical geometry are displayed.

## 1. INTRODUCTION

The reconciliation of theory and experiment in aqueous colloid science is often predicated on the availability of a suitable relationship between surface charge,  $\sigma$ , and surface potential,  $\Psi_0$ . When it proves necessary to complicate the model by the addition of a Stern-type region in the immediate neighbourhood of the particle surface, the required potential-charge relationship is that for the surface formed by the outer Helmholtz plane. This relationship is provided by solving the Poisson–Boltzmann equation,

$$\nabla^2 \Psi = \frac{4\pi e}{\epsilon} \sum_i n_i z_i \exp(-z_i e \Psi / kT) \quad (1.1)$$

for the electrostatic potential,  $\Psi$ , around the charged colloidal particle in an electrolyte solution where the bulk (number) concentration of ionic species,  $i$ , of valency  $z_i$ , is  $n_i$ . The appropriate equation connecting  $\sigma$  and  $\Psi_0$  is obtained from the boundary conditions

$$\Psi|_{\text{surface}} = \Psi_0 \quad (1.2)$$

$$(\nabla \Psi) \cdot \hat{n}|_{\text{surface}} = -\frac{4\pi}{\epsilon} \sigma \quad (1.3)$$

where  $\hat{n}$  is the outward unit normal vector to the surface.

This is usually a straightforward procedure when the size of the particle is such that

$$\kappa l \ll 1$$

or

$$\kappa l \gg 1 \quad (1.4)$$

† Present address: Department of Physical Chemistry, University of Melbourne, Parkville, Victoria, Australia.

where  $l$  is some characteristic dimension of the particle and

$$\kappa = \left( \frac{4\pi e^2}{\epsilon kT} \sum_i n_i z_i^2 \right)^{\frac{1}{2}}. \quad (1.5)$$

In the former case, the particle appears “point-like” in comparison to the extent of the double layer as measured by Debye screening length  $\kappa^{-1}$  and a linearization of the differential equation is a good approximation if the surface potential  $\Psi_0$  is not too large, *i.e.*,

$$\exp(-z_i e \Psi / kT) \rightarrow 1 - z_i e \Psi / kT. \quad (1.6)$$

In the latter case, the particle is large compared to the double layer thickness which can be regarded as a thin region around the particle surface. In this case, the curvature of the particle surface can be ignored and the non-linear Poisson-Boltzmann equation can be solved in planar geometry, *i.e.*,

$$\nabla^2 \rightarrow \frac{d^2}{dz^2} \quad (1.7)$$

where  $z$  is the distance normal to the particle surface.

For the majority of colloidal systems,  $\Psi_0$  and  $\kappa l$  are such that the differential eqn (1.1) cannot be well approximated either by linearizing or by assuming planar geometry. As most of these systems are spherical, the solution of the Poisson-Boltzmann equation in spherical geometry assumes a special importance. In what follows we restrict ourselves, for simplicity, to the case of a spherical colloidal particle immersed in a symmetrical  $z$ - $z$  electrolyte of (number) concentration,  $n_0$ , for which eqn (1.1) reduces to

$$\frac{d^2 \Psi}{dr^2} + \frac{2}{r} \frac{d\Psi}{dr} = \frac{8\pi n_0 e z}{\epsilon} \sinh(z e \Psi / kT) \quad (1.8)$$

and the boundary conditions become

$$\Psi|_a = \Psi_0 \quad (1.9)$$

$$\left. \frac{d\Psi}{dr} \right|_a = -\frac{4\pi}{\epsilon} \sigma. \quad (1.10)$$

In writing eqn (1.1) or (1.8) we have assumed the zero of electrostatic potential to be in the bulk electrolyte outside the double layer and therefore the potential  $\Psi$  must also satisfy the requirement

$$\Psi(r) \rightarrow 0 \quad \text{as } r \rightarrow \infty \quad (1.11)$$

An analytic solution to eqn (1.8) satisfying the boundary conditions (1.9), (1.10) and (1.11) has never been exhibited, although various numerical solutions have been given.<sup>1</sup> A number of approximate analytic techniques have been applied to the problem.

The earliest and most obvious approach is to attempt a perturbation solution<sup>2</sup> using as a zero'th approximation the solution

$$\Psi_L(r) = \Psi_0 \kappa a e^{\kappa a} \frac{e^{-\kappa r}}{\kappa r} \quad (1.12)$$

of the linearized PB equation,

$$\frac{d^2 \Psi}{dr^2} + \frac{2}{r} \frac{d\Psi}{dr} = \kappa^2 \Psi \quad (1.13)$$

where

$$\kappa^2 = \frac{8\pi n_0 e^2 z^2}{\epsilon kT}. \quad (1.14)$$

Recently Brenner and Roberts<sup>3</sup> showed that very good approximate solutions could be obtained by using a solution

$$\Psi(r) = \Psi_L(r)/[1 - \lambda \Psi_L^3(r)], \quad (1.15)$$

where the coefficient  $\lambda$  is determined by optimizing the solution  $\Psi(r)$  so as to minimize the system free energy.

An alternative approach is *via* the analogous planar Poisson-Boltzmann equation

$$\frac{d^2\Psi}{dz^2} = \frac{8\pi n_0 e z}{\epsilon} \sinh ze\Psi/kT \quad (1.16)$$

which has a solution  $\Psi_p(z)$  satisfying the boundary conditions at the particle surface given by

$$\Psi_p(z) = 2\left(\frac{kT}{ze}\right) \ln\left(\frac{1 + \gamma e^{-\kappa z}}{1 - \gamma e^{-\kappa z}}\right) \quad (1.17)$$

where

$$\gamma = \left(\frac{e^{ze\Psi_0/2kT} - 1}{e^{ze\Psi_0/2kT} + 1}\right). \quad (1.18)$$

Recently, Abraham-Shrauner<sup>4</sup> has obtained an approximate solution by a perturbation scheme which used the solution  $\Psi_p$  of the planar PB equation as the zero'th order solution.

As a general rule, approximate theories which start with the linearized solution  $\Psi_L(r)$  are limited to the small  $\kappa a$  regime. This solution implies that the particle is "point-like" when compared to the double layer, a condition well satisfied in the small  $\kappa a$  regime. The solution in the large  $\kappa a$  regime where the system is much more "plane-like" would require high order perturbation theory for accurate results. However, methods which start with the planar result  $\Psi_p(r)$  are for the same reasons restricted to the large  $\kappa a$  regime and furthermore deny the fact that, asymptotically, the form of the linearized spherical solution must hold, *i.e.*, at large  $r$ ,

$$\Psi(r) \sim e^{-\kappa r}/r. \quad (1.19)$$

The matching of this true long-range form with the short-range planar solution is a mathematical difficulty which the present theory attempts to alleviate. The variational approach of Brenner and Roberts avoids these limitations on the perturbation theory approaches at the expense of a physically *ad hoc* variational function (1.15) which requires a numerical minimization procedure and does not lend itself to use in approximate analytic theories.

The present theory utilizes the fact that sufficiently near to the surface of a sphere of any radius  $a$ , the potential  $\Psi(r)$  must look like the planar solution (1.17) but must go over, at large  $r$ , to the asymptotic result (1.19). It is possible to find a simple function  $\Psi(r)$  which has these properties as outlined in the next section, and to construct a suitable perturbation scheme to extend the range of validity of the solution into the small  $\kappa a$  regime.

## 2. THE ZERO'TH ORDER SOLUTION

To avoid carrying physical constants through the following calculations, we will use the reduced potential,  $Y$ , given by

$$Y = ze\Psi/kT \quad (2.1)$$

and the scaled radial distance,  $R$ , given by

$$R = \kappa r. \quad (2.2)$$

We will adopt throughout the convention that scaled variables are denoted by the capital. The spherical Poisson-Boltzmann eqn (1.8) becomes

$$\frac{d^2 Y}{dR^2} + \frac{2}{R} \frac{dY}{dR} = \sinh Y. \quad (2.3)$$

In order to obtain a form of the Poisson-Boltzmann equation suitable for a perturbation theory, we will introduce a new spherical variable,  $s$ , given by

$$s = \gamma A e^A e^{-R}/R \quad (2.4)$$

where  $\gamma$  is given by eqn (1.18), or in reduced quantities,

$$\gamma = \frac{e^{Y_0/2} - 1}{e^{Y_0/2} + 1} \quad (2.5)$$

where

$$Y_0 = ze\Psi_0/kT \quad (2.6)$$

and

$$A = \kappa a. \quad (2.7)$$

The range of the new variable is from zero ( $r = \infty$ ) to  $\gamma(r = a)$ . The boundary conditions can now be written as

$$Y(s)|_\gamma = Y_0 \quad (2.8)$$

$$\left. \frac{dY}{ds} \right|_\gamma = \left( \frac{4\pi ze}{\epsilon \kappa kT} \right) \left( \frac{A}{A+1} \right) \frac{\sigma}{\gamma} \quad (2.9)$$

where we have used the result

$$\frac{ds}{dR} = -\left( \frac{R+1}{R} \right) s. \quad (2.10)$$

The asymptotic behaviour of the exact solution (1.19) is now written as

$$Y(s) \sim s \quad (2.11)$$

as  $s \rightarrow 0$ . With this change of variable, the spherical Poisson-Boltzmann eqn (2.3) becomes

$$\left( \frac{1+R}{R} \right)^2 s^2 \frac{d^2 Y}{ds^2} + s \frac{dY}{ds} = \sinh Y \quad (2.12)$$

where  $(1+R/R)^2$  may be regarded as a known function of the new variable  $s$  via the defining relationship (2.4). The utility of eqn (2.12) as a form of the Poisson-Boltzmann equation about which to build a perturbation theory becomes obvious if we make analogous changes of variables in the planar Poisson-Boltzmann equation. In reduced units the planar Poisson-Boltzmann equation is

$$\frac{d^2 Y}{dZ^2} = \sinh Y \quad (2.13)$$

where

$$Z = \kappa z. \quad (2.14)$$

We introduce a new planar variable,  $P$ , defined by

$$P = \gamma e^{-z} \quad (2.15)$$

where  $\gamma$  is given by eqn (2.5). The range of this variable is from zero ( $z = \infty$ ) to  $\gamma(z = 0)$ , the identical range of the spherical variable  $s$ . The boundary conditions are

$$Y(P)|_{\gamma} = Y_0 \quad (2.16)$$

$$\left. \frac{dY}{dP} \right|_{\gamma} = \left( \frac{4\pi z e}{\epsilon \kappa k T} \right)_{\gamma} \sigma. \quad (2.17)$$

The asymptotic behaviour of the exact solution to the planar Poisson-Boltzmann equation is

$$Y(P) \sim P \quad (2.18)$$

as  $P \rightarrow 0$ . With this change of planar variable, the planar Poisson-Boltzmann equation becomes

$$P^2 \frac{d^2 Y}{dP^2} + P \frac{dY}{dP} = \sinh Y. \quad (2.19)$$

The solution of this equation satisfying the boundary conditions (2.16)–(2.18) is (from 1.17)

$$Y(P) = 2 \ln \left( \frac{1+P}{1-P} \right). \quad (2.20)$$

The solutions of the differential eqn (2.12) and (2.19) have identical boundary conditions and asymptotic requirements, and the independent variables ( $s, P$ ) have identical ranges. Moreover, as  $R \rightarrow \infty$

$$\left( \frac{R+1}{R} \right)^2 \rightarrow 1$$

and the differential equations become identical. If  $A (\kappa a)$  is large, then

$$\left( \frac{R+1}{R} \right)^2 \sim 1$$

for all  $R \geq A$ . This suggests that a good approximate solution of the spherical Poisson-Boltzmann equation (at least for large  $\kappa a$ ) might be

$$Y(s) = 2 \ln \left( \frac{1+s}{1-s} \right) \quad (2.21)$$

or, in terms of the usual variables,

$$Y(R) = 2 \ln \left( \frac{1 + \gamma A e^A e^{-R/R}}{1 - \gamma A e^A e^{-R/R}} \right). \quad (2.22)$$

For large  $R$ , this function has the asymptotic form required, *viz*,

$$Y(R) \simeq 4\gamma A e^A e^{-R/R}. \quad (2.23)$$

If we introduce the variable

$$Z = R - A,$$

then for  $Z \ll A$  (very near the particle surface),

$$Y(Z) \simeq 2 \ln \left( \frac{1 + \gamma e^{-z}}{1 - \gamma e^{-z}} \right) \quad (2.24)$$

to leading order in  $(Z/A)$ . This is the planar result which should be expected physically. Moreover, if the surface potential is small, then

$$\gamma \simeq Y_0/4 \ll 1 \quad (2.25)$$

and the function becomes

$$Y(R) \simeq Y_0 A e^A e^{-R}/R \quad (2.26)$$

for all  $R \geq A$ , which is the linearized Poisson-Boltzmann equation solution. That the function (2.21) is a good approximate solution to the spherical Poisson-Boltzmann equation for large  $\kappa a$  can be verified by comparison with the exact numerical solutions obtained by Loeb, Overbeek and Wiersema.<sup>1</sup> In general, the approximate solution lies below the exact result and the percentage deviation,  $\Delta(R)$ , defined by

$$\Delta(R) = 100 \left( \frac{Y_{\text{exact}}(R) - Y_{\text{approx}}(R)}{Y_{\text{exact}}(R)} \right) \quad (2.27)$$

will be positive as shown schematically in fig. 1(a). The form of the deviation curve as a function of  $\kappa r$  can be explained as follows: since both exact and approximate solutions start at  $Y_0$  for  $r = a$ , the percent deviation will start at zero and rise as  $r$  increases. The error reaches a maximum value since both exact and approximate

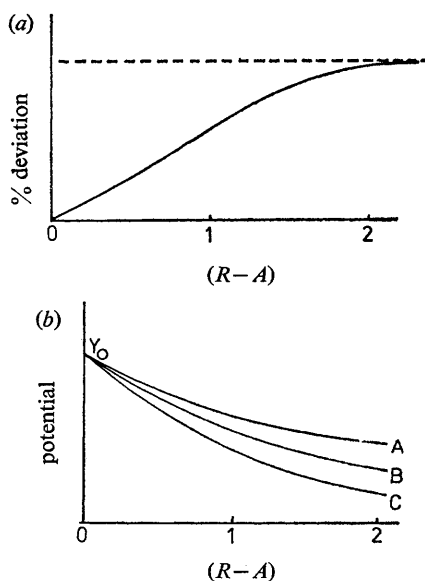


FIG. 1.—(a) Schematic plot of the percent deviation of the approximation solution (for a given  $Y_0$  and  $\kappa a$ ) as a function of  $\kappa r$ . (b) Schematic plot of the solution of the Poisson-Boltzmann equation in spherical geometry. (A) Linearized Debye-Hückel solution (2.26); (B) exact numerical solution; (C) present theory's zero'th order solution (2.22).

solutions have the same asymptotic form. Thus they differ only by a multiplicative constant at most for large  $r$ . The maximum percent deviation as a function of  $r$  occurs for  $R-A \gg 1$ . To exhibit the accuracy of the approximate solution, we calculate the maximum percent deviation  $\Delta_M$  for the solution corresponding to parameters  $Y_0$  and  $A$  ( $ze\Psi/kT$  and  $\kappa a$ ) by

$$\Delta_M(Y_0, A) = 100 \left| \frac{\bar{Y} - 4\gamma}{\bar{Y}} \right| \quad (2.28)$$

where  $\bar{Y}$  and  $4\gamma$  are the coefficients of  $Ae^A e^{-R}/R$  in the exact and zero'th order

approximate asymptotic solutions respectively. The quantity  $\bar{Y}(A, Y_0)$  has been obtained numerically by Loeb, Wiersema and Overbeek.<sup>1</sup> (They use the symbol  $Y$ ). We plot  $\Delta_M(Y_0, A)$  as a function of reduce surface potential  $Y_0$  for various values of  $A(\kappa a)$ . This is shown as the solid curves in fig. 2. We see that the maximum deviation is  $<10\%$  for all surface potentials provided  $\kappa a > 4$  and  $<2\%$  for all

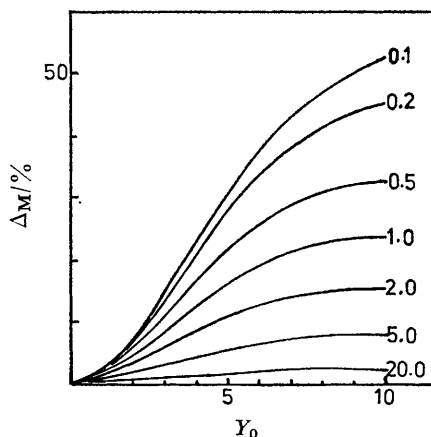


FIG. 2.—The maximum percent deviation  $\Delta_M$  of the zero'th order solution (2.22) relative to the exact numerical solution as a function of reduced surface potential,  $Y_0(zeY_0/kT)$  and  $\kappa a$ .

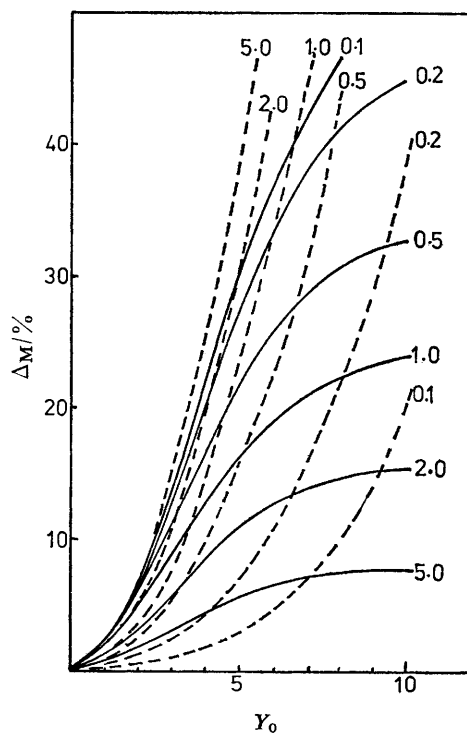


FIG. 3.—The maximum percent deviation  $\Delta_M$  for the zero'th order solution (2.15) compared with  $|\Delta_M|$  for the linear Debye-Huckel solution (2.20) (broken curves) as a function of reduced surface potential  $Y_0$  and  $\kappa a$ .

surface potentials provided  $\kappa a > 20$ . For small  $\kappa a$  values the deviation is  $< 10\%$  provided  $\Psi_0 < \sim 3kT/ze$ .

In fig. 3, the accuracy of the linearized solution (2.26) as measured by

$$\Delta_M^{\text{lin}}(Y_0, A) = 100 \frac{\bar{Y} - Y_0}{\bar{Y}} \quad (2.29)$$

is displayed (see broken curves) for comparison with the present theory (solid curves). We see that for  $\kappa a > 1$ , the present approximation is more accurate than the linearized solution for all values of the surface potential. As seen from fig. 1(b), the linear solution is an upper bound to the exact solution, while the present approximation is an underestimate for all values of  $\kappa a$  and  $\Psi_0$ . The error as measured by  $\Delta_M$  in using the linearized solution increases with surface potential as one would expect from the nature of the approximation. As the present theory contains the surface potential  $\Psi_0$  only in the factor  $\gamma$  (which is insensitive to  $\Psi_0$  as  $\Psi_0$  becomes large), the error levels off at large values of the surface potential. Therefore, the present zero'th order solution must become the better approximation for sufficiently large surface potentials for any  $\kappa a$ . This can be seen in fig. 3.

It must be pointed out that the maximum deviation is an overly pessimistic measure of the accuracy of the approximation, since it is the deviation in large  $\kappa r$  regime well away from the surface where the potential itself is small. In the neighbourhood of the surface where the potential can be large, the deviation is smaller. Thus integrals of the potential over the electrolyte volume, *e.g.*, the system free energy, will be in error by smaller amounts than the maximum deviation  $\Delta_M$  might suggest.

### 3. THE FIRST ORDER APPROXIMATION

Because the zeroth order solution (2.21) contains the characteristics of both the planar and asymptotic spherical solutions, one would expect that a low order perturbation theory would extend the region of validity of the approximate solution into the small  $\kappa a$  region. In this section we will develop a suitable perturbation scheme. Eqn (2.12) is first rearranged to facilitate this by dividing through by  $[(R+1)/R]^2$  to obtain

$$s^2 \frac{d^2 Y}{ds^2} + \left( \frac{R}{R+1} \right)^2 s \frac{dY}{ds} = \left( \frac{R}{R+1} \right)^2 \sinh Y. \quad (3.1)$$

A perturbation parameter  $\lambda$  is then introduced into this equation by writing

$$\left( \frac{R}{R+1} \right)^2 = 1 - \lambda \left( \frac{2R+1}{(R+1)^2} \right). \quad (3.2)$$

The solution of this resultant equation,  $Y_\lambda(s)$ , will be the solution of the spherical Poisson-Boltzmann equation for  $\lambda = 1$ . We now seek a solution

$$Y_\lambda(s) = Y_0(s) + \lambda y(s) \quad (3.3)$$

where

$$Y_0(s) = 2 \ln \left( \frac{1+s}{1-s} \right) \quad (3.4)$$

is the zero'th order solution examined in the previous section, satisfying

$$s^2 \frac{d^2 Y_0(s)}{ds^2} + s \frac{dY_0(s)}{ds} = \sinh Y_0(s).$$



Substituting eqn (3.3) and (3.2) into (3.1) and retaining terms to first order in the perturbation parameter  $\lambda$ , we obtain

$$s^2 \frac{d^2 y}{ds^2} + s \frac{dy}{ds} - y \cosh Y_0(s) = -\left(\frac{2R+1}{(R+1)^2}\right) s^2 \frac{d^2 Y_0(s)}{ds^2}. \quad (3.5)$$

From eqn (3.4) we have that

$$\cosh Y_0(s) = \frac{1+6s^2+s^4}{(1-s^2)^2} \quad (3.6)$$

$$s^2 \frac{d^2 Y_0(s)}{ds^2} = \frac{8s^3}{(1-s^2)^2} \quad (3.7)$$

so that the differential equation for the first order correction  $y(s)$  to the zero'th order solution,  $Y_0(s)$ , can be written

$$\frac{d^2 y}{ds^2} + \frac{1}{s} \frac{dy}{ds} - \frac{1+6s^2+s^4}{s^2(1-s^2)^2} y = -\frac{8s}{(1-s^2)^2} \frac{2R+1}{(R+1)^2}. \quad (3.8)$$

To solve this equation we must first examine the homogeneous equation

$$\left(\frac{d^2}{ds^2} + \frac{1}{s} \frac{d}{ds} - \frac{1+6s^2+s^4}{s^2(1-s^2)^2}\right) y = 0. \quad (3.9)$$

If we attempt a series solution to this equation, we can derive a first solution

$$y_1(s) = \frac{s}{1-s^2}. \quad (3.10)$$

That  $y_1(s)$  satisfies the differential eqn (3.9) may be readily proved by substitution. Given a first solution to the differential equation, a second can be found by seeking a solution in the form<sup>5</sup>

$$y_2(s) = v(s) y_1(s). \quad (3.11)$$

The function  $v(s)$  satisfies the differential equation

$$\frac{d^2 v}{ds^2} + \frac{dv}{ds} \left( \frac{1}{s} + \frac{2 dy_1(s)/ds}{y_1(s)} \right) = 0 \quad (3.12)$$

obtained by substituting eqn (3.11) into (3.9). A first integral of eqn (3.12) yields

$$\frac{dv}{ds} = \frac{1}{y_1^2(s)} \exp \left( - \int^s \frac{ds}{s} \right) \quad (3.13)$$

$$= \frac{(1-s^2)^2}{s^3}. \quad (3.14)$$

Therefore

$$v(s) = \frac{1}{2} \left( s^2 - \frac{1}{s^2} - 4 \ln s \right). \quad (3.15)$$

With a knowledge of  $y_1(s)$  and  $y_2(s)$ , two independent solutions of the homogeneous differential equation, we can construct the particular solution of the inhomogeneous eqn (3.8) in the form<sup>5</sup>

$$\int^s dt \frac{f(t)}{W(t)} [y_1(t)y_2(s) - y_1(s)y_2(t)], \quad (3.16)$$

where

$$f(t) = -\frac{8t}{(1-t^2)^2} \left( \frac{2R(t)+1}{(R(t)+1)^2} \right), \quad (3.17)$$

where  $R$  is a function of  $t$  via the relation

$$t = \gamma A e^A e^{-R}/R \quad (3.18)$$

and the Wronskian  $W(t)$  is given by

$$W(t) = \left[ y_1(t) \frac{dy_2(t)}{dt} - \frac{dy_1(t)}{dt} y_2(t) \right] \quad (3.19)$$

$$= y_1^2(t) \frac{dv(t)}{dt}. \quad (3.20)$$

The general solution of eqn (3.8) can, therefore, be written as

$$y(s) = Cy_1(s) + Dy_2(s) - 8y_1(s) \int^s dt \left( \frac{2R+1}{(R+1)^2} \right) \frac{t^3}{(1-t^2)^3} [v(s) - v(t)] \quad (3.21)$$

The constants  $C$  and  $D$  are chosen to match the appropriate boundary conditions. To first order in the perturbation parameter  $\lambda$  the total potential is ( $\lambda = 1$ )

$$Y(s) = Y_0(s) + y(s). \quad (3.22)$$

Since  $Y_0(s)$  has already been chosen to satisfy the boundary condition (2.8), we must have that

$$y(s)|_\gamma = 0. \quad (3.23)$$

Since  $Y_0(s) \sim s$  for  $s$  near zero, the asymptotic requirement (2.11) on the solution  $Y(s)$  will also apply to  $y(s)$ , viz,

$$y(s) \sim s \quad (3.24)$$

for small  $s$ . With no loss of generality, we may replace the indefinite integral in eqn (3.21) by the definite integral

$$I(s) = \int_0^s dt \left( \frac{2R+1}{(R+1)^2} \right) \frac{t^3}{(1-t^2)^3} [v(s) - v(t)]. \quad (3.25)$$

Although

$$v(t) \sim \frac{1}{t^2} \quad (3.26)$$

for small  $t$ , the  $t^3$  factor in the integrand will ensure that the integral (3.25) will converge. The general solution is now

$$y(s) = Cy_1(s) + Dy_2(s) - 8y_1(s)I(s). \quad (3.27)$$

From eqn (3.25) we have that

$$I(s) \xrightarrow{s \rightarrow 0} 0 \quad (3.28)$$

so that the third term in eqn (3.27) goes to zero faster than  $s$  and is therefore asymptotically acceptable. Similarly, the first term satisfies the asymptotic requirement (3.24), since

$$y_1(s) \sim s \quad (3.29)$$

for small  $s$ . However, because of the asymptotic behaviour in eqn (3.26) of  $v(s)$  near

$s = 0$ , the second term does not satisfy the requirement (3.24). Indeed,  $y_2(s)$  diverges, *i.e.*,

$$y_2(s) \sim \frac{1}{s} \quad (3.30)$$

for small  $s$ . The constant  $D$  must therefore be zero. Thus a solution  $y(s)$  satisfying the asymptotic restriction (3.24) is

$$y(s) = Cy_1(s) - 8y_1(s)I(s). \quad (3.31)$$

From the boundary condition (3.23) we have

$$\begin{aligned} C &= 8I(\gamma) \\ &= 8 \int_0^\gamma dt \left( \frac{2R+1}{(R+1)^2} \right) \frac{t^3}{(1-t^2)^3} (v(\gamma) - v(t)). \end{aligned} \quad (3.32)$$

We note that  $C$  is a function of both  $\gamma$  and  $A$ .

The total first order solution to the spherical Poisson–Boltzmann equation is then,

$$Y(s) = 2 \ln \left( \frac{1+s}{1-s} \right) + \frac{8s}{1-s^2} [I(\gamma) - I(s)] \quad (3.33)$$

where the function  $I(s)$  is given by eqn (3.25). The asymptotic behaviour of the first order approximation is therefore

$$Y(s) \simeq (4+C)s, \quad (3.34)$$

or in terms of the usual variables,

$$Y(R) \simeq (4+C)\gamma A e^A e^{-R}/R. \quad (3.35)$$

From eqn (3.15), we see that  $v(s)$  is a negative, monotonic increasing function of  $s$  in the range  $0 \rightarrow 1$ . Thus the integrand in the integral (3.25) defining  $I(s)$  is positive over the integration range. This is sufficient to prove that  $I(s)$  is a positive monotonic increasing function. Thus

$$I(\gamma) - I(s) > 0,$$

and therefore the first order correction  $y(s)$  has the same sign as the zero'th order solution  $Y_0(s)$ . Since we have shown in section 2 that  $Y_0(s)$  is an underestimate of the exact solution, the first order solution (3.33) will prove a better solution to the spherical Poisson–Boltzmann equation.

In fig. 4, we plot the relative error in the asymptotic forms (as was done in the previous section),

$$\Delta_M(Y_0, A) = 100 \left( \frac{\bar{Y} - (4+C)\gamma}{\bar{Y}} \right) \quad (3.36)$$

for the first order approximation (3.33). The quantity  $I(\gamma)$  [and in general  $I(s)$ ] could be expressed in terms of known functions, but in view of the simplicity of the integrand defining  $I(s)$ , the most rapid and accurate way of calculating it is to perform a numerical integration by machine. A fifty-point Simpson's rule was used for these calculations. We see from fig. 4 that the first order approximate solution is a good approximation for all surface potentials, provided  $\kappa a > 1$ .

In fig. 5, we plot the quantity  $C(Y_0, A)$  as a function of surface potential and  $\kappa a$ . This quantity is useful in colloidal systems where one wishes to know the asymptotic potential profile using a better approximation than the linearized approximation.

For example, a calculation of the interaction potential of two spherical colloidal particles in the overlap approximation could make use of the asymptotic form [eqn (3.35)] instead of the linearized form [eqn (1.12)], which is not good for large potentials and  $\kappa a > 2$ .

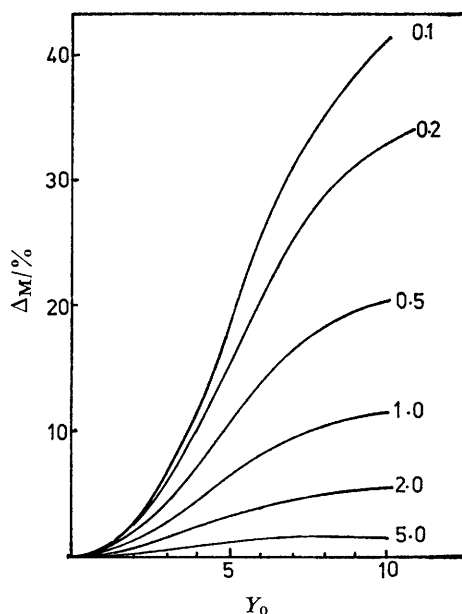


FIG. 4.—The maximum percent deviation  $\Delta_M$  of the first order solution to the spherical PB equation relative to the exact numerical solution as a function of reduced surface potential and  $\kappa a$ .

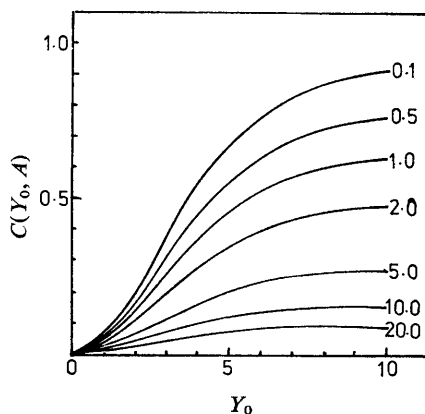


FIG. 5.—The quantity  $C$  as given by eqn (3.32) which occurs in the large  $R$  asymptotic expression  $Y_1(R)$  [eqn (3.35)] as a function of reduced surface potential and  $\kappa a$ .

#### 4. CHARGE AND FREE ENERGY RELATIONSHIPS

In this section we derive expressions for the surface charge  $\sigma$  and free energy per unit area  $F$  of the spherical colloidal in  $z$ - $z$  electrolyte as functions of the surface potential  $\Psi_0$  and  $\kappa a$ . In terms of reduced quantities, we have [from eqn (2.9)]

$$\sigma = \left( \frac{\epsilon \kappa k T}{4\pi z e} \right) \left( \frac{A+1}{A} \right)^\gamma \frac{dY}{ds} \Big|_\gamma. \quad (4.1)$$

The surface charge is therefore a function of the surface potential (through  $\gamma$ ) and  $\kappa a$ . We also have for the free energy per unit area,<sup>1</sup>

$$F = -\left(\frac{kT}{ze}\right) \int_0^{Y_0} \sigma(\kappa a, Y_0) dY_0 \quad (4.2)$$

$$= -\left(\frac{\epsilon\kappa}{\pi}\right) \left(\frac{kT}{ze}\right)^2 \left(\frac{A+1}{A}\right) \int_\gamma^1 \frac{dY}{ds} \bigg|_\gamma \frac{\gamma d\gamma}{1-\gamma^2} \quad (4.3)$$

where the integration variable has been changed from  $Y_0$  to  $\gamma$  using eqn (2.5).

The zero'th order relationship between surface charge and surface potential is obtained by substituting  $Y_0(s)$  for  $Y(s)$  in eqn (4.1). From eqn (3.3) we have

$$\frac{dY_0}{ds} \bigg|_\gamma = \frac{4}{1-\gamma^2} \quad (4.4)$$

and, therefore, from eqn (4.1),

$$\sigma^{(0)} = \left(\frac{\kappa a + 1}{\kappa a}\right) \sigma_P \quad (4.5)$$

where

$$\begin{aligned} \sigma_P &= \left(\frac{\epsilon\kappa kT}{4\pi ze}\right) \frac{4\gamma}{1-\gamma^2} \\ &= \left(\frac{\epsilon\kappa kT}{2\pi ze}\right) \sinh(ze\Psi_0/2kT) \end{aligned} \quad (4.6)$$

is the planar charge relation. It follows immediately from eqn (4.2) that the zero'th order free energy relationship is given by

$$F^{(0)} = \left(\frac{1+\kappa a}{\kappa a}\right) F_P \quad (4.7)$$

where

$$F_P = -\frac{\epsilon\kappa}{\pi} \left(\frac{kT}{ze}\right)^2 [\cosh(ze\Psi_0/2kT) - 1] \quad (4.8)$$

is the free energy per unit surface area in planar geometry.

In fig. 6, we plot the percentage error  $\Delta_\sigma$  in the calculation of the surface charge

$$\Delta_\sigma(Y_0, A) = 100 \left| \frac{\sigma_{\text{exact}} - \sigma_{\text{approx}}}{\sigma_{\text{exact}}} \right| \quad (4.9)$$

for the zero'th order approximation (4.5) (solid curves) and the linearized approximation (broken curves)

$$\sigma_{\text{DH}} = \frac{\epsilon\kappa}{4\pi} \Psi_0 \left(\frac{1+\kappa a}{\kappa a}\right) \quad (4.10)$$

as a function of  $Y_0$  and  $\kappa a$ . The exact surface charge is obtained from the numerical tables of Loeb *et al.*<sup>1</sup> [in their symbols  $I(q_0, y_0)$ ]. The magnitude of the surface charge is overestimated in the zero'th order approximation presented here and underestimated in the linearized approximation. Note that eqn (4.5) reduces to (4.10) in the limit of small  $\Psi_0$ .

In fig. 7 we plot the percentage deviation between the approximate, theoretical and exact, numerical free energies  $\Delta_F$ , defined by

$$\Delta_F = 100|[F(\text{exact}) - F(\text{theory})/F(\text{exact})]| \quad (4.11)$$

as a function of  $Y_0$  and  $\kappa a$  for the zero'th order approximation (4.7) and the linearized approximation

$$F_{\text{DH}} = -\frac{\epsilon\kappa}{8\pi}\Psi_0^2\left(\frac{1+\kappa a}{\kappa a}\right). \quad (4.12)$$

Note that eqn (4.7) reduces to eqn (4.12) in the limit that  $\Psi_0$  is small. From fig. 7 we see that for  $\kappa a > 1$ , the zero'th order relation (4.7) is a better approximation than the linear approximation (4.12) for all values of the surface potential. Note that, in general, the linearized free energy is an underestimate to the exact free energy, while the present theory is an overestimate.

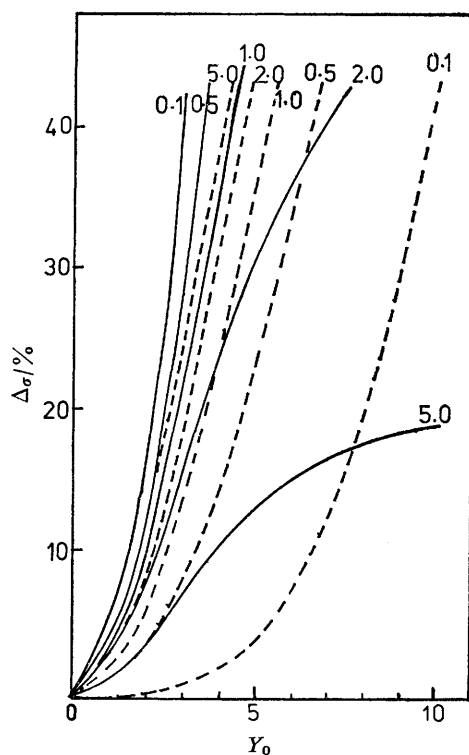


FIG. 6.—The percentage error  $\Delta_\sigma$  between the approximate theoretical and exact numerical surface charge density as a function of reduced surface potential  $Y_0$  and  $\kappa a$  for the zero'th order expression (4.5) (solid curves) and the linearized expression (4.10) (broken curves).

The first order charge relationship is obtained by substituting the first order solution (3.33) for  $Y(s)$  in eqn (4.1). Since, to this order,

$$\begin{aligned} \left. \frac{dY}{ds} \right|_\gamma &= \left. \frac{dY_0}{ds} \right|_\gamma + 8 \left. \frac{d}{ds} \left\{ \frac{s}{1-s^2} [I(\gamma) - I(s)] \right\} \right|_\gamma \\ &= \left. \frac{dY_0}{ds} \right|_\gamma - \left. \frac{\gamma}{1-\gamma^2} \frac{dI(s)}{ds} \right|_\gamma. \end{aligned} \quad (4.13)$$

From eqn (3.25), we see that

$$\left. \frac{dI(s)}{ds} \right|_y = \frac{(1-\gamma^2)^2}{\gamma^3} \int_0^\gamma dt \frac{t^3}{(1-t^2)^3} \left[ \frac{2R+1}{(R+1)^2} \right] \quad (4.14)$$

where we have made use of eqn (3.14). The first order charge relationship is then

$$\sigma^{(1)} = \sigma^{(0)} - \left( \frac{2\epsilon\kappa kT}{\pi ze} \right) \left( \frac{A+1}{A} \right) \left( \frac{1-\gamma^2}{\gamma} \right) \int_0^\gamma dt \frac{t^3}{(1-t^2)^3} \left( \frac{2R+1}{(R+1)^2} \right) \quad (4.15)$$

$$= \sigma^{(0)} \left\{ 1 - 2 \left( \frac{(1-\gamma^2)^2}{\gamma^2} \right) \int_0^\gamma dt \frac{t^3}{(1-t^2)^3} \left( \frac{2R+1}{(R+1)^2} \right) \right\} \quad (4.16)$$

where  $\sigma^{(0)}$  is the zero'th order relation given by eqn (4.5). Since  $\sigma^{(0)}$  is an overestimate to the exact surface charge, one would expect  $\sigma^{(1)}$  as given by eqn (4.16) to correct this. In fig. 8 we plot the percentage error  $\Delta_\sigma$  for the first order approximation (4.16) to the surface charge [see eqn (4.9)] as a function of reduced surface

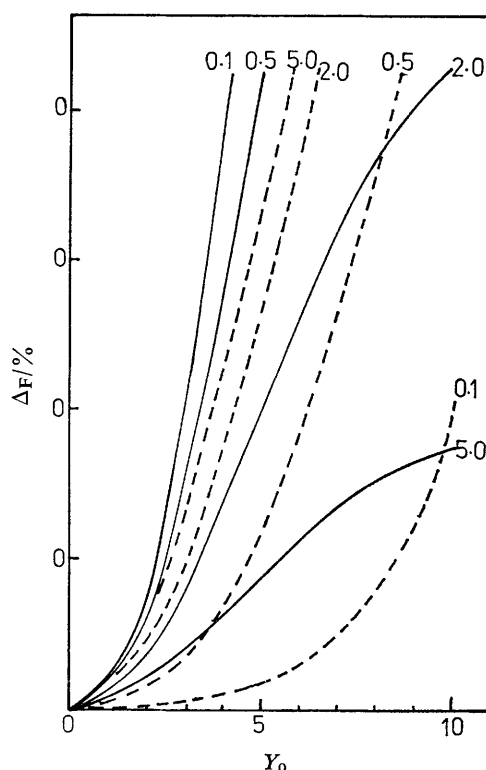


FIG. 7.—The percentage deviation  $\Delta_F$  between the approximate, theoretical and exact, numerical free energies as a function of reduced surface potential  $Y_0$  and  $\kappa a$  for the zero'th order result (4.7) (solid curves) and the linearized result (4.12) (broken curves).

potential and  $\kappa a$ . From fig. 8, we see that  $\sigma^{(1)}$  is a good estimate of the true surface charge ( $\Delta_\sigma < 2\%$ ) for all potentials provided  $\kappa a > 5.0$ . The integral in eqn (4.16) was calculated with a 50-point Simpson's rule integration.

## 592 POISSON-BOLTZMANN EQUATION FOR A COLLOIDAL PARTICLE

The first order free energy relationship is obtained by substituting eqn (4.13) and (4.14) into eqn (4.3). We obtain

$$F^{(1)} = F^{(0)} + 8 \left( \frac{\epsilon \kappa}{\pi} \right) \left( \frac{kT}{ze} \right)^2 \left( \frac{A+1}{A} \right) \int_0^\gamma \frac{d\gamma}{\gamma} \int_0^\gamma dt \frac{t^3}{(1-t^2)^3} \left( \frac{2R+1}{(R+1)^2} \right) \quad (4.17)$$

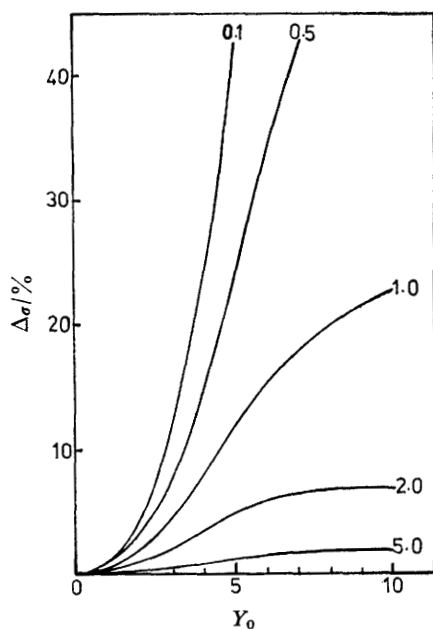


FIG. 8.—The percentage error  $\Delta_\sigma$  between the first order surface charge expression (4.16) and the exact numerical surface charge as a function of reduced surface potential  $Y_0$  and  $\kappa a$ .

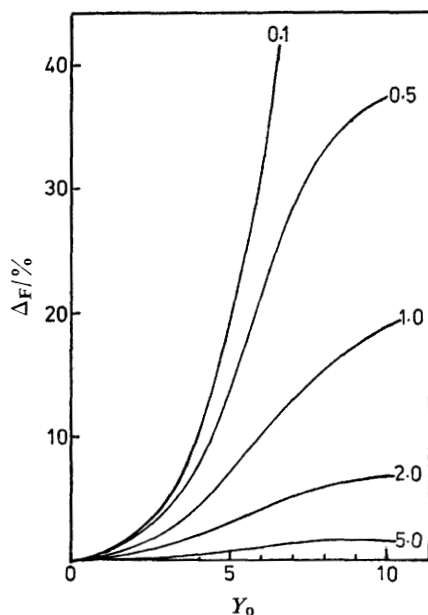


FIG. 9.—The percentage deviation  $\Delta_F$  of the first order free energy [eqn (4.18)] from the exact numerical free energy as calculated by Loeb *et al.*<sup>1</sup> as a function of reduced surface potential  $Y_0$  and  $\kappa a$ .



which may be written as

$$F^{(1)} = F^{(0)} \left\{ 1 - \left( \frac{1-\gamma^2}{\gamma^2} \right) \int_0^\gamma dt \frac{t^3}{(1-t^2)^2} \left( \frac{2R+1}{(R+1)^2} \right) \right\} \quad (4.18)$$

after performing the integration over  $\gamma$ . Since  $F^{(0)}$  was shown to be an over-estimate of the true free energy, the first order expression (4.18) would be expected to correct for this. In fig. 9, we plot the percentage deviation  $\Delta_F$  for this first order expression for the free energy per unit area [see eqn (4.11)] as a function of  $Y_0$  and  $\kappa a$ . From fig. 9 we see the substantial improvement in  $\Delta_F$ . The first order approximation (4.18) is a good approximation for all surface potentials for  $\kappa a > 5$ .

## 5. DISCUSSION

The approach adopted in this paper is directly applicable to the case of unsymmetrical electrolytes, and other geometries. For a  $z$ - $z'$  electrolyte a solution to the planar Poisson-Boltzmann equation can usually be found, since a first integral of that equation can always be made. This will provide the functional basis from which the perturbation theory can be derived. The essential step in the process is the change of variable from the fundamental distance variable to the variable which has the form of the solution of the linearized Poisson-Boltzmann equation in that geometry.

To illustrate this technique in another geometry, we consider the case of an infinite cylinder of radius  $a$  immersed in  $z$ - $z$  electrolyte. In reduced units, the Poisson-Boltzmann equation is

$$\frac{d^2 Y}{d\rho^2} + \frac{1}{\rho} \frac{dY}{d\rho} = \sinh Y \quad (5.1)$$

where  $\rho$  is the radial distance variable (scaled with respect to  $\kappa$ ) measured from the cylinder axis. The linearized PB equation,

$$\frac{d^2 Y}{d\rho^2} + \frac{1}{\rho} \frac{dY}{d\rho} = Y, \quad (5.2)$$

has the asymptotically acceptable solution

$$Y(\rho) = \frac{Y_0}{K_0(A)} K_0(\rho) \quad (5.3)$$

where  $K_0(\rho)$  is the zero order modified Bessel function of the second kind.<sup>6</sup> Asymptotically,<sup>6</sup>

$$K_\nu(\rho) \xrightarrow{\rho \rightarrow \infty} \sqrt{\frac{\pi}{2\rho}} e^{-\rho}. \quad (5.4)$$

We make the change of variable from  $\rho$  to the new cylindrical variable,  $C$ , defined by

$$C = \gamma \frac{K_0(\rho)}{K_0(A)} \quad (5.5)$$

with a range of zero ( $\rho = \infty$ ) to  $\gamma(\rho = A)$ . The cylindrical Poisson-Boltzmann equation becomes

$$\left( \frac{K_1(\rho)}{K_0(\rho)} \right)^2 C^2 \frac{d^2 Y}{dC^2} + C \frac{dY}{dC} = \sinh Y \quad (5.6)$$

and the boundary conditions become

$$Y(C)|_{\gamma} = Y_0 \quad (5.7)$$

$$\left. \frac{dY}{dC} \right|_{\gamma} = \left( \frac{4\pi ze}{\epsilon \kappa kT} \right) \frac{K_0(A)}{K_1(A)} \frac{\sigma}{\gamma} \quad (5.8)$$

where we have used the result <sup>6</sup>

$$\frac{dK_0(\rho)}{d\rho} = -K_1(\rho). \quad (5.9)$$

We have also the asymptotic requirement

$$Y(C) \sim C \quad (5.10)$$

for small  $C$ . The ratio  $[K_1(\rho)/K_0(\rho)]$  has the properties <sup>6</sup>

$$K_1(\rho)/K_0(\rho) > 1 \quad (5.11)$$

for  $\rho > 0$ ,

$$K_1(\rho)/K_0(\rho) \xrightarrow{\rho \rightarrow \infty} 1 \quad (5.12)$$

$$\xrightarrow{\rho \rightarrow 0} \infty. \quad (5.13)$$

Thus this function of  $C$  has the same properties in cylindrical geometry as  $(R+1)/R$  has in the spherical geometry discussed in previous sections. By analogous arguments to those used in section 2, a zero'th order solution of the cylindrical Poisson-Boltzmann equation valid for large  $\kappa a$  is

$$Y_0(C) = 2 \ln \left( \frac{1+C}{1-C} \right) \quad (5.14)$$

$$= 2 \ln \left( \frac{1+\gamma \frac{K_0(\rho)}{K_0(A)}}{1-\gamma \frac{K_0(\rho)}{K_0(A)}} \right) \quad (5.15)$$

satisfying the boundary and asymptotic conditions (5.7) and (5.10). By dividing eqn (5.6) by  $[K_1(\rho)/K_0(\rho)]^2$  and introducing the perturbation parameter  $\lambda$  by writing

$$\left( \frac{K_0(\rho)}{K_1(\rho)} \right)^2 = 1 - \lambda \left( \frac{K_1^2(\rho) - K_0^2(\rho)}{K_1^2(\rho)} \right) \quad (5.16)$$

in the resultant equation, we can find a first order solution

$$Y_1(C) = 2 \ln \left( \frac{1+C}{1-C} \right) + \frac{8C}{1-C^2} [\mathcal{L}(\gamma) - \mathcal{L}(C)], \quad (5.17)$$

where

$$\mathcal{L}(C) = \int_0^C dt \left( \frac{K_1^2(\rho) - K_0^2(\rho)}{K_1^2(\rho)} \right) \frac{t^3}{(1-t^2)^3} [v(C) - v(t)] \quad (5.18)$$

where  $v(t)$  is the function defined by eqn (3.15) and  $\rho$  is that function of  $t$  defined by

$$t = \gamma \frac{K_0(\rho)}{K_0(A)}. \quad (5.19)$$

The charge and free energy relations at zero'th order are then

$$\sigma^{(0)} = \frac{K_1(\kappa a)}{K_0(\kappa a)} \sigma_p \quad (5.20)$$

$$F^{(0)} = \frac{K_1(\kappa a)}{K_0(\kappa a)} F_p \quad (5.21)$$

where  $\sigma_p$  and  $F_p$  are the corresponding planar quantities [see eqn (4.6) and (4.8)]. At first order,

$$\sigma^{(1)} = \sigma^{(0)} \left\{ 1 - 2 \frac{(1-\gamma^2)^2}{\gamma^2} \int_0^\gamma dt \frac{t^3}{(1-t^2)^3} \left[ \frac{K_1^2(\rho) - K_0^2(\rho)}{K_1^2(\rho)} \right] \right\} \quad (5.22)$$

$$F^{(1)} = F^{(0)} \left\{ 1 - \left( \frac{1-\gamma^2}{\gamma^2} \right) \int_0^\gamma dt \frac{t^3}{(1-t^2)^2} \left[ \frac{K_1^2(\rho) - K_0^2(\rho)}{K_1^2(\rho)} \right] \right\} \quad (5.23)$$

where the integrations may be performed numerically when required.

The present method also sheds light on the surprising fact that the solution to the linearized Poisson-Boltzmann equation is a remarkably good approximation to the exact solution for  $\kappa a < 1$  for values of the surface potential where

$$\sinh Y_0 \gg Y_0$$

(see fig. 3). This is at first sight rather difficult to understand. However, if we rewrite eqn (3.1) as

$$s^2 \frac{d^2 Y}{ds^2} = \left( \frac{R}{R+1} \right)^2 \left( \sinh Y - s \frac{dY}{ds} \right), \quad (5.24)$$

we see that the r.h.s. is small for  $R$  near  $A (< 1)$  (provided the potential  $Y$  is not too large) by virtue of the  $(R/R+1)^2$  factor. For large  $R$ , the asymptotic form of  $Y(s)$  will hold and the r.h.s. will be small by virtue of the  $(\sinh Y - s dY/ds)$  factor. A zero'th order solution is obtained by putting the r.h.s. to zero, viz,

$$s^2 \frac{d^2 Y}{ds^2} = 0, \quad (5.25)$$

which has the solution

$$Y^{(0)}(s) = \frac{Y_0}{\gamma} s \quad (5.26)$$

$$= Y_0 A e^A e^{-R/R}, \quad (5.27)$$

satisfying the boundary and asymptotic conditions (2.8) and (2.11). A first-order perturbation correction to the linearized solution (5.26) can be obtained by writing

$$\text{r.h.s.} = \lambda \left( \frac{R}{R+1} \right)^2 \left( \sinh Y - s \frac{dY}{ds} \right) \quad (5.28)$$

and seeking a solution

$$Y^{(1)}(s) = Y^{(0)}(s) + \lambda y(s). \quad (5.29)$$

The correction  $y(x)$  satisfies the differential equation (to first order in  $\lambda$ )

$$s^2 \frac{d^2 y}{ds^2} = \left( \frac{R}{R+1} \right)^2 \left( \sinh Y^{(0)} - s \frac{dY^{(0)}}{ds} \right) \quad (5.30)$$

$$= \left( \frac{R}{R+1} \right)^2 \left( \sinh \frac{Y_0 s}{\gamma} - \frac{Y_0 s}{\gamma} \right). \quad (5.31)$$

By similar arguments to those developed in section 3, a general solution to eqn (5.31) is

$$y(s) = D + Es + \int^s dt \left( \frac{R(t)}{R(t)+1} \right)^2 \left[ \sinh \left( \frac{Y_0 t}{\gamma} \right) - \left( \frac{Y_0 t}{\gamma} \right) \right] \left( \frac{s-t}{t^2} \right) \quad (5.32)$$

where  $R(t)$  is a function of  $t$  via eqn (3.18). The solution satisfying the boundary and asymptotic conditions (3.23) and (3.24) is

$$= J(s) - J(\gamma)(s/\gamma) \quad (5.33)$$

where the function  $J(s)$  is given by

$$J(s) = \int_0^s dt \left( \frac{R}{R+1} \right)^2 \left[ \sinh \left( \frac{Y_0 t}{\gamma} \right) - \left( \frac{Y_0 t}{\gamma} \right) \right] \left( \frac{s-t}{t^2} \right). \quad (5.34)$$

The first-order solution

$$Y^{(1)}(s) = \left( \frac{Y_0 - J(\gamma)}{\gamma} \right) s + J(s) \quad (5.35)$$

will serve to extend the range of validity of the linearized solution (5.26) into the large  $(Y_0, A)$  regimes.

The perturbation scheme outlined herein may be formally extended to higher order quite easily but the inevitable complication of the resultant solutions will probably make their use impractical.

The author gratefully acknowledges the Commonwealth Scientific and Industrial Research Organisation of Australia for the award of a travelling postdoctoral fellowship, and the S.R.C. for financial support; also Prof. R. H. Ottewill for his encouragement and support during the author's stay at Bristol University.

<sup>1</sup> (a) A. L. Loeb, J. Th. G. Overbeek and P. H. Wiersema, *The Electrical Double Layer around a Spherical Colloidal Particle* (M.I.T. Press, Cambridge, Mass., 1961); (b) H. Muller, *Kolloidchem. Beih.*, 1923, **26**, 257; (c) N. E. Hoskin and S. Levine, *Phil. Trans. Roy. Soc. A*, 1956, **248**, 433.

<sup>2</sup> T. H. Gronwall, V. K. La Mer and K. Sandved, *Phys. Z.*, 1928, **29**, 358.

<sup>3</sup> S. L. Brenner and R. E. Roberts, *J. Phys. Chem.*, 1973, **77**, 2367.

<sup>4</sup> B. Abraham-Schrauner, *J. Colloid Interface Sci.*, 1973, **44**, 79.

<sup>5</sup> P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill, N.Y., 1953), vol. I, p. 523.

<sup>6</sup> M. Abramowitz and I. A. Stegun, *A Handbook of Mathematical Functions* (Dover, N.Y., 1965).