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Properties of a Double Layer with Asymmetric Electrolytes: Cylindrical and Spherical Particles with an Ion-Penetrable Membrane

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We consider a particle coated with a membrane immersed in an arbitrary *a*:*b* electrolyte solution. The membrane bears homogeneously distributed fixed charges and is penetrable to electrolytes. In particular, cylindrical and spherical particles are examined. The approximate analytical expressions for the thermodynamic properties of the system under consideration, including Helmholtz free energy, entropy, and the amount of co-ion adsorption, are derived. We show that if the radius of a particle is large enough, the present semianalytical treatment yields satisfactory results. Under typical conditions, the deviation from the exact value is on the order of 5%. If the curvature approaches zero, the present result reduces to the approximate solution for a planar geometry, and, if the thickness of the membrane approaches zero, it reduces to the approximate solution for a rigid charged surface and becomes the exact solution for the case of symmetric electrolytes.

Key Words: charged membrane; asymmetric electrolytes; Poisson–Boltzmann equation; thermodynamic properties; cylindrical and spherical particles.

I. INTRODUCTION

The distribution of the electrical potential for a charged surface immersed in an electrolyte solution is governed by the Poisson–Boltzmann equation (PBE). Solving this equation is a prerequisite to the estimation of the essential thermodynamic properties of the system under consideration (1). The difficulty in the resolution of a PBE depends largely on the shape of the surface, the associated boundary conditions, and the type of electrolyte. More often than not, drastic assumptions are made so that PBE can either be solved analytically or an approximate solution can be obtained. These include planar surface, low surface potential, constant surface potential or constant surface charge density, and symmetric electrolytes. In the past two decades, attempts have been made to reflect, more realistically, the situation in practice through the form of PBE and the associated boundary conditions. In the case of biological cells and some artificial membranes, for instance, there exists a surface layer near the solid–liquid interface. This layer contains fixed charges due to factors such as the dissociation of the functional groups it bears, and is penetrable to electrolytes in the bulk liquid phase (2). As an example, the peripheral zone of human erythrocyte contains a glycoprotein layer about 15 nm thick. This layer possesses some ionogenic groups and forms the outer boundary of the lipid layer (3, 4). Apparently, the classic rigid wall model is inappropriate for the description of the physical properties of erythrocyte.

In a series of works presented by Ohshima *et al.* (5–7), the electrostatic potential distribution for a membrane immersed in an electrolyte solution is analyzed. The membrane bears fixed charges and is ion penetrable. This model mimics closely a biological cell and some artificial membranes, and therefore its result is of fundamental significance in practice. The model of Ohshima *et al.* (6) is extended to the case of an arbitrary *a*:*b* electrolyte in a recent study by Hsu and Kuo (8). In addition to the electrostatic potential distribution, approximate analytical expressions for the properties of a double layer, including Helmholtz free energy, entropy, and surface excess of co-ion, are derived.

Although most of the analytical results for PBE are based on a planar surface, its solution for a nonplanar surface is highly desirable in practice. Unfortunately, due to the difficulty involved in the solution procedure, available results are extremely limited, especially for asymmetric electrolytes. In a recent study, we show that this can be circumvented by conducting a semiempirical analysis (9). The approximate analytical result obtained is reasonably accurate under typical conditions. In the present study, this approach is adopted for the estimation of the essential thermodynamic properties of a nonplanar particle coated with a charged membrane immersed in an arbitrary *a*:*b* electrolyte solution. In particular, cylindrical and spherical particles are considered.

II. ANALYSIS

The system under consideration is shown in Fig. 1. A cylindrical or spherical particle coated with an ion-penetrable membrane of finite thickness is immersed in an *a*:*b* electrolyte solution. The membrane contains a certain amount of

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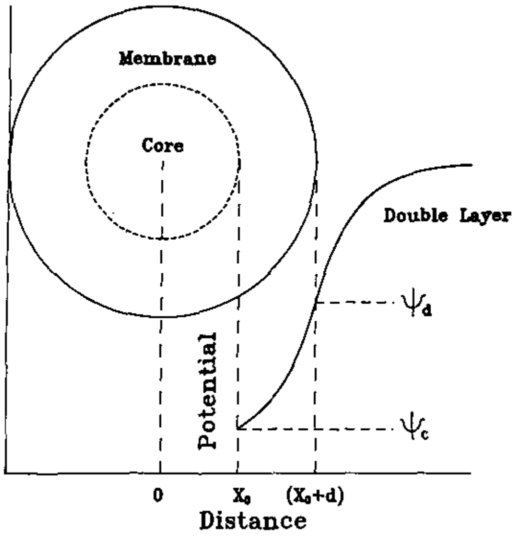

FIG. 1. A schematic representation of the system under consideration: d is the dimensionless thickness of membrane, and ψ_d and ψ_c are, respectively, the dimensionless potential at the membrane–liquid interface and at the outer boundary of the uncharged core.

fixed charges due to, for example, the dissociation of the functional groups it bears. Without loss of generality, we assume that these fixed charges are negative. For simplicity, the fixed charges are assumed to distribute uniformly in the membrane.

The electrical potential distribution is described by the Poisson equation

$$\frac{1}{X^m}\frac{d}{dX}\left(X^m\frac{d\psi}{dX}\right)=\frac{g}{a+b}, \quad (X_0+d)<X<\infty \qquad [1]$$

$$\frac{1}{X^m}\frac{d}{dX}\left(X^m\frac{d\psi}{dX}\right)=\frac{g+N}{a+b}, \quad X_0<X<(X_0+d), \qquad [2]$$

where $\psi = e\phi/k_BT$, $g = [\exp(b\psi)-\exp(-a\psi)]$, $X = \kappa r$, $\kappa^2 = e^2a(a+b)n_a^0/\epsilon_0\epsilon_r k_BT$, *and* $N = ZN_0N_A/an_a^0$. In these expressions, ϕ is the electrostatic potential; d denotes the dimensionless thickness of the membrane; N_0 and Z are, respectively, the density and the valence of the charged groups in the membrane ($-ZeN_0$ is the density of the fixed space charge, e being the elementary charge); N_A represents the Avogadro number; ϵ_r and ϵ_0 are the relative permittivity of the solution and the vacuum, respectively; n_a^0 is the number concentration of cation in the bulk liquid phase; κ and k_B are, respectively, the reciprocal Debye length and the Boltzmann constant; T is the absolute temperature; r represents the distance measured from either the axis of a cylinder or the center of a sphere; and m denotes the geometry parameter ($m = 0$ for a flat plate, $m = 1$ for a cylinder, and $m = 2$ for a sphere). The boundary conditions associated with Eqs. [1] and [2] are

$$\psi \to 0 \text{ and } (d\psi/dX) \to 0 \text{ as } X \to \infty \qquad [2a]$$

$$\psi(X_0+d)^- = \psi(X_0+d)^+ = \psi_d \qquad [2b]$$

$$(d\psi/dX)_{X\to(X_0+d)^-} = (d\psi/dX)_{X\to(X_0+d)^+} \qquad [2c]$$

$$\psi \to \psi_c \text{ and } (d\psi/dX) = 0 \text{ as } X \to X_0. \qquad [2d]$$

In these expressions X_0 denotes the dimensionless size of the uncharged core of a particle, and ψ_d and ψ_c represent, respectively, the dimensionless electrostatic potential at the membrane–liquid interface and at the outer boundary of the uncharged core.

2.1. *Distribution of the Potential Gradient in a Double Layer*

Suppose that the derivative of ψ with respect to X can be expressed by (10, 11)

$$d\psi/dX = H(\psi, X) = \sum_{i=0}^{n} c_i(\psi)/X^i. \qquad [3]$$

Then, it can be shown that [1] and [2a] lead to the approximate result (Appendix A)

$$\frac{d\psi}{dX} = \left(\frac{2}{a+b}\right)^{1/2}\left[\frac{1}{b}(e^{b\psi}-1)+\frac{1}{a}(e^{-a\psi}-1)\right]^{1/2} - \frac{1}{X}\frac{2m}{a}\tanh(a\psi/4) + \frac{1}{X^2} \times\left[\frac{m^2\tanh^2(a\psi/4) - 4m(m-1)\ln[\cosh(a\psi/4)]}{ak_3\sinh(a\psi/2)}\right], \qquad [4]$$

where

$$k_3 = \begin{cases}[(k-2)k_1+2k_2]/k, & \text{if } k \leqslant 4\\ [2k_1+(k-2)k_2]/k, & \text{if } k > 4\end{cases} \qquad [4a]$$

$$k_1 = 2/\{(k)^{1/2}[(k/2)^{2/(k-2)}-1]\} \qquad [4b]$$

$$k_2 = 2/k^{1/2} \qquad [4c]$$

$$k = 2 + 2b/a. \qquad [4d]$$

Here, k is a measure of the degree of asymmetry of electrolytes (12).

2.2. *Distribution of the Potential Gradient in a Membrane*

Similar to the treatment of [1], we assume that

$$d\psi/dX = H(\psi, X) = \sum_{i=0}^{n} d_i(\psi)/X^i. \qquad [5]$$

Substituting this expression into [2] yields

$$H\left(\frac{\partial H}{\partial \psi}\right)_X + \left(\frac{\partial H}{\partial X}\right)_\psi + \frac{mH}{X} = \frac{g+N}{a+b} = 0,$$

$$X_0 < X < X_0 + d. \quad [6]$$

Collecting terms of the same order in X leads to the set of equations

$$d_0 d_0' = (g+N)/(a+b) \quad [7a]$$

$$d_0 d_1' + d_1 d_0' + m d_0 = 0 \quad [7b]$$

$$d_0 d_2' + d_1 d_1' + d_2 d_0' + (m-1) d_1 = 0 \quad [7c]$$

$$\cdots$$

where the differentiation is with respect to ψ. The boundary conditions associated with these equations are

$$d_i = c_i \text{ at } \psi = \psi_\mathrm{d} \text{ (or } X \to X_0 + d\text{)}, \; i = 0, 1, 2, \ldots. \quad [8]$$

Solving [7a] through [7c] subject to [8] gives the variation of function $H(\psi, X)$ or $d\psi/dX$ across the membrane. It can be shown that (Appendix B)

$$\frac{d\psi}{dX} = d_0 + \frac{d_1}{X} + \frac{d_2}{X^2} + \cdots, \quad [9]$$

where

$$d_0 = \left(\frac{2}{a+b}\right)^{1/2}\left[\frac{1}{b}(e^{b\psi} - 1) + \frac{1}{a}(e^{-a\psi} - 1) + N(\psi - \psi_\mathrm{d})\right]^{1/2} = (2/aY)(f_1/k)^{1/2} \quad [9a]$$

$$d_1 = \frac{2}{a(f_1^{1/2}/Y)}\left[u_0 \ln\left(\frac{Y}{Y_\mathrm{d}}\right) + \sum_{i=1}^{n_1} \frac{u_i}{i}(Y^i - Y_\mathrm{d}^i) + \frac{2mk_3}{a}\left(\frac{Y_\mathrm{d} + Y_\mathrm{d}^{-1} - 2}{2}\right)\right] \quad [9b]$$

$$d_2 = \frac{2}{a(f_1^{1/2}/Y)}\left[v_0 \ln\left(\frac{Y}{Y_\mathrm{d}}\right) + \sum_{i=1}^{n_2} \frac{v_i}{i}(Y^i - Y_\mathrm{d}^i)\right.$$
$$\left. + \frac{[m(Y_\mathrm{d} - 1)/(Y_\mathrm{d} + 1)] - 4m(m-1)\ln[(Y_\mathrm{d}^{1/2} - Y_\mathrm{d}^{-1/2})/2]}{k_3(Y_\mathrm{d} - Y_\mathrm{d}^{-1})}\right] \quad [9c]$$

$$Y = \exp(a\psi/2), \quad [9d]$$

where f_1, Y_d, u_i, and v_i are defined in Appendix B.

2.3. *Estimation of ψ_{Don} and $\psi_d = \psi_d(\psi_{Don})$*

If $d \gg 1$, ψ remains constant at ψ_Don, the dimensionless Donnan potential, for $X < X_0$. Two of the boundary conditions associated with [2] are

$$\psi_\mathrm{c} \to \psi_\mathrm{Don} \text{ and } \frac{d}{dX}\left(X^m \frac{d\psi}{dX}\right) = 0 \text{ as } X \to X_0. \quad [10a]$$

Since the core of a particle ($X < X_0$) is free of fixed charge, and is impenetrable to electrolyte, the right-hand side of [2] vanishes, and [2] and [10a] lead to

$$Y_\mathrm{Don}^k + NY_\mathrm{Don} - 1 = 0, \quad [10b]$$

where $Y_\mathrm{Don} = \exp(a\psi_\mathrm{Don}/2)$. Solving this equation directly is almost impossible. However, a quick estimation for its solution can be obtained through an iterative procedure (Appendix C). By [9] and [10a] we have

$$d_0(\psi_\mathrm{Don}) + \frac{d_1(\psi_\mathrm{Don})}{X_0} + \frac{d_2(\psi_\mathrm{Don})}{X_0^2} + \cdots = 0. \quad [11]$$

This equation describes the relation between ψ_d and ψ_Don. It can be shown that an approximate solution to Eq. [11] is (Appendix C)

$$\psi_\mathrm{d} \simeq \psi_\mathrm{d,3} = \psi_\mathrm{Don} + \frac{1}{N}\left\{\frac{1}{b}(\exp(b\psi_\mathrm{Don}) - 1) + \frac{1}{a}(\exp(-a\psi_\mathrm{Don}) - 1) - \frac{a+b}{2}\left[\frac{d_1(\psi_\mathrm{Don})_2}{X_0} + \frac{d_2(\psi_\mathrm{Don})_2}{X_0^2}\right]^2\right\}, \quad [12]$$

where $d_1(\psi_\mathrm{Don})_2$ and $d_2(\psi_\mathrm{Don})_2$ are defined in Appendix C.

2.4. *Double-Layer Properties*

Since the charges are distributed within the membrane, the surface charge density defined in the conventional analysis for a rigid surface is inappropriate for the present case. Here we assume that the total or apparent charge density σ_t ($= -ZeN_0 d\kappa^{-1}$; see Appendix D) comprises two parts: an equivalent charge density due to the fixed charges distributed in the membrane, σ_sl, and the charge density at the membrane–liquid interface, σ_dl. The former is the charge density obtained by distributing uniformly all the fixed charges in the membrane over a surface located somewhere in the range $[X_0, X_0 + d]$. We have

$$\sigma_\mathrm{t} = \sigma_\mathrm{sl} + \sigma_\mathrm{dl}. \quad [13]$$

Define the dimensionless interface charge density p_dl as

$$p_\mathrm{dl} = -ae\sigma_\mathrm{dl}/2k_3\epsilon_0\epsilon_r k_B T\kappa. \quad [14]$$

It can be shown that, regardless of the geometry of a particle (9),

$$\sigma_{\mathrm{dl}} = -\epsilon_0\epsilon_{\mathrm{r}}\frac{\kappa k_{\mathrm{B}}T}{e}\left(\frac{d\psi}{dX}\right)_{X=X_0+d} \quad [14\mathrm{a}]$$

Equations [4], [14], and [14a] yield

$$p_{\mathrm{dl}} = \frac{a}{2k_3}\left(\frac{d\psi}{dX}\right)_{X=X_0+d}$$

$$= -\sinh(a\psi_{\mathrm{d}}/2) - \frac{1}{X_0+d}\frac{m}{k_3}\tanh(a\psi_{\mathrm{d}}/4) + \frac{1}{(X_0+d)^2}\frac{m^2\tanh^2(a\psi_{\mathrm{d}}/4) - 4m(m-1)\ln[\cosh(a\psi_{\mathrm{d}}/4)]}{2k_3^2\sinh(a\psi_{\mathrm{d}}/2)}. \quad [14\mathrm{b}]$$

2.4.1. Helmholtz free energy. The Helmholtz free energy comprises the free energy due to the double layer, F_{eld}, and that due to membrane, F_{els} (8); i.e.,

$$F_{\mathrm{el}} = F_{\mathrm{eld}} + F_{\mathrm{els}}, \quad [15]$$

where

$$F_{\mathrm{eld}} = \int_0^{\sigma_{\mathrm{dl}}}\phi(\sigma'_{\mathrm{dl}})d\sigma'_{\mathrm{dl}} \quad [15\mathrm{a}]$$

$$F_{\mathrm{els}} = \int_{\sigma_{\mathrm{dl}}}^{\sigma_{\mathrm{t}}}\phi_{\mathrm{Don}}(\sigma'_{\mathrm{t}})d\sigma'_{\mathrm{t}}. \quad [15\mathrm{b}]$$

In these expressions, ϕ_{d} and ϕ_{Don} are, respectively, the potential at $X = X_0 + d$ and that at $X = X_0$. Employing [12], [14b], and [10b], we obtain

$$F_{\mathrm{el}} = \left(\frac{2k_{\mathrm{B}}T}{ae}\right)^2\epsilon_0\epsilon_{\mathrm{r}}\kappa k_3\Bigg\{[p_{\mathrm{dl}}\ln(p_{\mathrm{dl}}+q_{\mathrm{dl}}) - q_{\mathrm{dl}} + 1] - \frac{m}{k_3(X_0+d)}\ln\left(\frac{q_{\mathrm{dl}}+1}{2}\right) + \frac{1}{(X_0+d)^2} \times\left[\frac{m}{2k_3}\frac{(q_{\mathrm{dl}}-1)(q_{\mathrm{dl}}+2)}{q_{\mathrm{dl}}(q_{\mathrm{dl}}+1)} - \frac{m(m-1)}{2k_3^2}\int_v^1\frac{\ln Z_1}{Z_1-1}dZ_1\right]\Bigg\} - \sigma_{\mathrm{dl}}\left(\frac{2k_{\mathrm{B}}T}{ae}\right)\ln Y_{\mathrm{Don}} + d\kappa^{-1}n_a^0k_{\mathrm{B}}T\Bigg[2\ln Y_{\mathrm{Don}} + Y_{\mathrm{Don}}^{-2} + \frac{2}{k-2}Y_{\mathrm{Don}}^{-2} - Y_{\mathrm{Don}}'^{-2} - \frac{2}{k-2}Y_{\mathrm{Don}}'^{k-2}\Bigg], \quad [15\mathrm{c}]$$

where

$$F_{\mathrm{eld}} = \left(\frac{2k_{\mathrm{B}}T}{ae}\right)^2\epsilon_0\epsilon_{\mathrm{r}}\kappa k_3\Bigg\{[p_{\mathrm{dl}}\ln(p_{\mathrm{dl}}+q_{\mathrm{dl}}) - q_{\mathrm{dl}} + 1] - \frac{m}{k_3(X_0+d)}\ln\left(\frac{q_{\mathrm{dl}}+1}{2}\right) + \frac{1}{(X_0+d)^2}\left[\frac{m}{2k_3}\frac{(q_{\mathrm{dl}}-1)(q_{\mathrm{dl}}+2)}{q_{\mathrm{dl}}(q_{\mathrm{dl}}+1)} - \frac{m(m-1)}{2k_3^2}\int_v^1\frac{\ln Z_1}{Z_1-1}dZ_1\right]\Bigg\} \quad [15\mathrm{d}]$$

$$F_{\mathrm{els}} = -\sigma_{\mathrm{dl}}\left(\frac{2k_{\mathrm{B}}T}{ae}\right)\ln Y_{\mathrm{Don}} + d\kappa^{-1}n_a^0k_{\mathrm{B}}T\Bigg[2\ln Y_{\mathrm{Don}} + Y_{\mathrm{Don}}^{-2} + \frac{2}{k-2}Y_{\mathrm{Don}}^{-2} - Y_{\mathrm{Don}}'^{-2} - \frac{2}{k-2}Y_{\mathrm{Don}}'^{k-2}\Bigg] \quad [15\mathrm{e}]$$

$$q_{\mathrm{dl}} = (p_{\mathrm{dl}}^2 + 1)^{1/2} \quad [15\mathrm{f}]$$

$$v = 2/(q_{\mathrm{dl}} + 1) \quad [15\mathrm{g}]$$

$$\int_v^1\frac{\ln Z_1}{Z_1-1}dZ = \sum_{i=1}^{\infty}\frac{v^i}{i^2} - \frac{\pi^2}{6} + \ln(v)\ln(1-v). \quad [15\mathrm{h}]$$

In [15c] and [15e], Y'_{Don} is the value of Y calculated at the Donnan potential in which the total surface charge density is regarded as σ_{dl}, not σ_{t}, i.e., $Y'_{\mathrm{Don}} = Y_{\mathrm{Don}}(\sigma_{\mathrm{dl}})$.

2.4.2. Amount of co-ion adsorption. From the thermodynamic point of view, the electrical Helmholtz free energy can be evaluated by

$$dF_{\mathrm{el}} = -\Gamma_+d\mu_+ - \Gamma_-d\mu_-, \quad [16]$$

where Γ_+ and Γ_- are the amount of adsorbed counterion and co-ion, respectively, and μ_+ and μ_- are the corresponding chemical potentials. For an ideal solution, we have

$$d\mu_+ = d\mu_- = 2k_{\mathrm{B}}TN_{\mathrm{A}}d\ln\kappa. \quad [17]$$

The electroneutrality requires that

$$a\Gamma_+ - b\Gamma_- + \sigma_{\mathrm{t}}/N_{\mathrm{A}}e = 0. \quad [18]$$

Equations [16], [17], and [18] lead to

$$\Gamma = \Gamma_- = -\frac{2}{kN_{\mathrm{A}}}\left(\frac{\sigma_{\mathrm{t}}}{ae} + \frac{\kappa}{2k_{\mathrm{B}}T}\frac{\partial F_{\mathrm{el}}}{\partial\kappa}\right). \quad [19]$$

Substituting [15c] into [19], we have

$$\Gamma = -2\kappa^{-1}n_a^0N_{\mathrm{A}}^{-1}k_3D_{\mathrm{dl}} - \frac{2}{kN_{\mathrm{A}}}\left(\frac{\sigma_{\mathrm{sl}}}{ae} + \frac{\kappa}{2k_{\mathrm{B}}T}\frac{\partial F_{\mathrm{els}}}{\partial\kappa}\right), \quad [20]$$

where

$$\begin{aligned} D_{\mathrm{dl}} = {} & p_{\mathrm{dl}} + 1 - q_{\mathrm{dl}} + \frac{1}{(X_0 + d)} \frac{m}{k_3} \frac{q_{\mathrm{dl}} - 1}{q_{\mathrm{dl}}} + \frac{1}{(X_0 + d)^2} \\ & \times \left\{ \frac{m^2}{4k_3^2} \left[-1 - \frac{2}{q_{\mathrm{dl}}(q_{\mathrm{dl}} + 1)} + \frac{2}{q_{\mathrm{dl}}^3} \right] + \frac{m(m-1)}{2k_3^2} \right. \\ & \left. \times \left[\frac{2}{q_{\mathrm{dl}}} \ln\left(\frac{q_{\mathrm{dl}} + 1}{2} \right) + \int_v^1 \frac{\ln Z_1}{Z_1 - 1} \, dZ_1 \right] \right\} \end{aligned} \qquad [20a]$$

$$\begin{aligned} \frac{\partial F_{\mathrm{els}}}{\partial \kappa} = {} & d\kappa^{-1} k_{\mathrm{B}} T \frac{\partial n_a^0}{\partial \kappa} \left[2 \ln Y_{\mathrm{Don}} + Y_{\mathrm{Don}}^{-2} \right. \\ & \left. + \frac{2}{k-2} Y_{\mathrm{Don}} - Y'^{2}_{\mathrm{Don}} - \frac{2}{k-2} Y'^{k-2}_{\mathrm{Don}} \right] \\ & + d_\kappa^{-1} k_{\mathrm{B}} T n_a^0 \left[\left(\frac{1}{2} Y_{\mathrm{Don}}^{-1} - 2 Y_{\mathrm{Don}}^{-3} + 2 Y_{\mathrm{Don}}^{-3} \right) \right. \\ & \left. \times \frac{\partial Y_{\mathrm{Don}}}{\partial \kappa} + (2 Y'^{-3}_{\mathrm{Don}} - 2 Y'^{k-3}_{\mathrm{Don}}) \frac{\partial Y'_{\mathrm{Don}}}{\partial \kappa} \right] \\ & - \frac{2 \sigma_{\mathrm{dl}} k_{\mathrm{B}} T}{ae} \times Y'_{\mathrm{Don}} \frac{\partial Y'_{\mathrm{Don}}}{\partial \kappa} \end{aligned} \qquad [20b]$$

$$\partial n_a^0 / \partial \kappa = 2 n_a^0 / \kappa \qquad [20c]$$

$$\frac{\partial Y_{\mathrm{Don}}}{\partial \kappa} = \frac{-Y_{\mathrm{Don}}^2}{k Y_{\mathrm{Don}}^{-1} + 2 N Y_{\mathrm{Don}}} \frac{\partial N}{\partial \kappa} \qquad [20d]$$

$$\frac{\partial Y'_{\mathrm{Don}}}{\partial \kappa} = \frac{-Y'^{2}_{\mathrm{Don}}}{k Y'^{k-1}_{\mathrm{Don}} + 2 N' Y'_{\mathrm{Don}}} \frac{\partial N'}{\partial \kappa} \qquad [20e]$$

$$\partial N / \partial \kappa = -2N / \kappa \qquad [20f]$$

$$\partial N' / \partial \kappa = -2N' / \kappa \qquad [20g]$$

$$\frac{N'}{N} = \frac{N'_0}{N_0} = \frac{\sigma_{\mathrm{dl}}}{\sigma_{\mathrm{t}}} = \frac{2 k_3 \epsilon_0 \epsilon_{\mathrm{r}} k_{\mathrm{B}} T \kappa \sinh(a\psi_d/2)}{-Z e^2 N_0 a d / \kappa}. \qquad [20h]$$

The reference state for the Helmholtz free energy is chosen as the state of an uncharged surface. Here, N'_0 is the fixed space charge density defined by $N_0 \sigma_{\mathrm{dl}} / \sigma_{\mathrm{t}}$, and N' is the value of N based on N'_0.

2.4.3. Entropy. The entropy of a double-layer S_{el} can be calculated by

$$S_{\mathrm{el}} = (\partial F_{\mathrm{el}} / \partial T)_{n_i}. \qquad [21]$$

It can be shown that

$$\begin{aligned} S_{\mathrm{el}} = {} & \frac{-3}{2} \frac{F_{\mathrm{eld}}}{T} - \left(\frac{k_{\mathrm{B}}}{ae} \right)^2 2 T \epsilon_0 \epsilon_{\mathrm{r}} \kappa k_3 \left\{ p_{\mathrm{dl}} \ln(q_{\mathrm{dl}} - p_{\mathrm{dl}}) \right. \\ & + \frac{m}{k_3 (X_0 + d)} \times \frac{q_{\mathrm{dl}} - 1}{q_{\mathrm{dl}}} - \frac{1}{(X_0 + d)^2} \\ & \times \left[\frac{m^2}{k_3^2} \left(\frac{2}{q_{\mathrm{dl}}(q_{\mathrm{dl}} + 1)} - \frac{1}{q_{\mathrm{dl}}^2} \right) + \frac{m(m-1)}{k_3^2} \right. \\ & \left. \left. \times \frac{\ln((q_{\mathrm{dl}} + 1)/2)}{q_{\mathrm{dl}}} \right] \right\} - 2 \sigma_{\mathrm{dl}} (k_{\mathrm{B}}/ae) \ln Y'_{\mathrm{Don}} \\ & + d\kappa^{-1} n_a^0 k_{\mathrm{B}} \times \left[2 \ln Y_{\mathrm{Don}} + Y_{\mathrm{Don}}^{-2} + \frac{2}{k-2} Y_{\mathrm{Don}}^{k-2} \right. \\ & \left. - Y'^{-2}_{\mathrm{Don}} + \frac{2}{k-2} Y'^{k-2}_{\mathrm{Don}} \right]. \end{aligned} \qquad [22]$$

III. DISCUSSION

For a charged surface immersed in an electrolyte solution, the Helmholtz free energy is calculated by

$$F_{\mathrm{el}} = \int_0^{\sigma_0} \phi_0(\sigma'_0) d\sigma'_0, \qquad [23]$$

where σ_0 and ϕ_0 are, respectively, the surface charge density and the surface potential. Since ϕ_0 does not exist in the present case, the exact value of the Hemholtz free energy, and hence the exact value of entropy, are not defined. The exact value of the amount of ion adsorption Γ_i can be calculated by

$$\Gamma_i = \int_V (n_i - n_i^0) d\mathbf{r} / A N_{\mathrm{A}}, \qquad [24]$$

where n_i and n_i^0 are the number concentration of species i and of species i in the bulk liquid phase, respectively; $\mathbf{r}$ denotes the position vector; V is the volume of the system; and A represents the surface area of the membrane. Figure 2 shows the variation in the amount of ion adsorption as a function of parameter k, defined in [4d]. Both the approximate value based on the present analysis and the exact value are presented in this figure. The average deviation in the amount of ion adsorption is summarized in Table 1. Figure 2 and Table 1 suggest that the deviation of the result estimated by the present method from the corresponding exact value is within a reasonable range.

The effect of the relative thickness of the uncharged core of a particle, X_0, on the performance of the present approximate result is illustrated in Fig. 3. This figure reveals that, although the deviation increases with the decrease in X_0, it is less than 5% if X_0 is greater than 2. Since this is usually satisfied in practice, the performance of the present approach is satisfactory.

3.1. Limiting Cases

In certain circumstances the present approximate formulas approach some of our previous results (8, 9, 12).

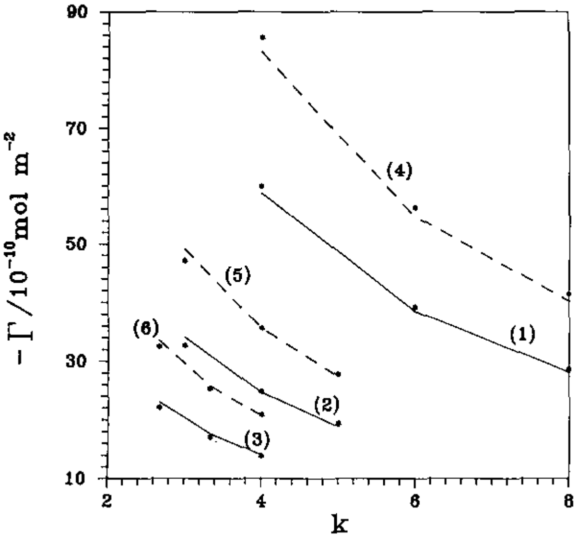

FIG. 2. Variation in the amount of ion adsorption as a function of parameter k. Ionic strength = $10^{-3}\,M$, $T = 298.15$ K, $\epsilon_0 = 78$, $X_0 = 2$, $d = 1$, $Z = 1$, and $N_0 = 10^{-3}\,M$. Solid line, exact value for $m = 1$ (cylinder); dashed line, exact value for $m = 2$ (sphere); *, present approximate result. Curves 1 and 4, $a = 1$; curves 2 and 5, $a = 2$; curves 3 and 6, $a = 3$.

3.1.1. Rigid surface. If $d \to 0$, the charged membrane reduces to a charged rigid surface. In this case, the governing equation becomes

$$\frac{1}{X^m}\frac{d}{dX}\left(X^m\frac{d\psi}{dX}\right) = \frac{g}{a+b}, \quad X_0 < X < \infty, \qquad [25]$$

with boundary conditions

$$\psi = \psi_0 \quad \text{at } X = X_0 \qquad [25a]$$

$$\psi \to 0 \quad \text{and} \quad d\psi/dX \to 0 \quad \text{as } X \to \infty. \qquad [25b]$$

The solution to [25] subject to [25b] is [4], with $X_0 < X < \infty$. Equations [14] and [14b] lead to

$$\begin{aligned} p_1 &= -ae\sigma_t/2k_3\epsilon_0\epsilon_r k_B T\kappa \\ &= -\sinh(a\psi_0/2) - \frac{1}{X_0}\frac{m}{k_3}\tanh(a\psi_0/4) \\ &\quad + \frac{1}{X_0^2}\,\frac{m^2\tanh^2(a\psi_0/4) - 4m(m-1)\ln[\cosh(a\psi_0/4)]}{ak_3^2\sinh(a\psi_0/2)}, \qquad [26] \end{aligned}$$

where p_1 is the dimensionless surface charge density and ψ_0 denotes the dimensionless potential at the solid–liquid interface. Equations [15c], [20], and [22] become, respectively,

TABLE 1
Average Deviation (%) in the Amount of Ion Adsorption for the Case Shown in Fig. 2

	$m = 1$	$m = 2$
$a = 1$	2.00	3.02
$a = 2$	2.67	1.68
$a = 3$	2.72	1.92

$$\begin{aligned} F_{el} = \left(\frac{2k_B T}{ae}\right)^2 \epsilon_0\epsilon_r\kappa k_3 \Bigg\{ &[-p_1\ln(p_1+q_1) - q_1 + 1] \\ &- \frac{m}{k_3X_0}\ln\left(\frac{q_1+1}{2}\right) + \frac{1}{X_0^2}\left[\frac{m}{2k_3^2}\frac{(q_1-1)(q_1+2)}{q_1(q_1+1)}\right. \\ &\left. - \frac{m(m-1)}{2k_3^2}\int_v^1 \frac{\ln Z_1}{Z_1-1}\,dZ_1\right]\Bigg\} \qquad [27] \end{aligned}$$

$$\Gamma = -2\kappa^{-1}n_a^0 N_A^{-1}k_3 D, \qquad [28]$$

where

$$\begin{aligned} D = p_1 + 1 - q_1 &+ \frac{1}{X_0}\frac{m}{k_3}\frac{q_1-1}{q_1} \\ &- \frac{1}{X_0^2}\left\{\frac{m^2}{4k_3^2}\left[1 + \frac{2}{q_1(q_1+1)} + \frac{2}{q_1}\right]\right. \\ &\left. - \frac{m(m-1)}{2k_3^2}\left[\frac{2}{q_1}\ln\left(\frac{q_1+1}{2}\right) + \int_v^1 \frac{\ln Z_1}{Z_1-1}\,dZ_1\right]\right\} \qquad [28a] \end{aligned}$$

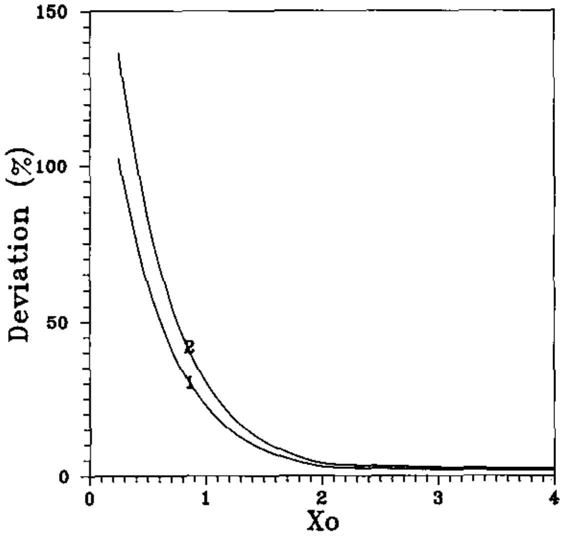

FIG. 3. The effect of the relative thickness of the uncharged core of a particle on the performance of the present approximate result. Values are the same as in Fig. 2, except that $X_0/d = 2$ and $m = 1$. Curve 1, $a{:}b = 1{:}2$; curve 2, $a{:}b = 2{:}1$.

$$S_{\mathrm{el}} = \frac{-3}{2}\frac{F_{\mathrm{el}}}{T} - \left(\frac{k_{\mathrm{B}}}{ae}\right)^2 2T\epsilon_0\epsilon_r\kappa k_3\Bigg\{p_1\ln(q_1 - p_1) + \frac{m}{k_3X_0} \times \frac{q_1 - 1}{q_1} - \frac{1}{X_0^2}\left[\frac{m^2}{k_3^2}\left(\frac{2}{q_1(q_1+1)} - \frac{1}{q_1^2}\right) + \frac{m(m-1)}{k_3^2} \times \frac{\ln((q_1+1)/2)}{q_1}\right]\Bigg\}, \quad [29]$$

where $q_1^2 = (p_1^2 + 1)$. If $m = 0$ (or $X_0 \to \infty$), the terms involving $1/X^i$, $i \geqslant 1$, in the perturbation expansion of $H(\psi, X)$ vanish, and [26] through [29] reduce to the expressions for a rigid planar surface (12). Furthermore, if $a = b$, these expressions become the exact results (12).

3.1.2. Planar surface. If $m = 0$ (or $X_0 \to \infty$), the terms involving $1/X_0^i$, $i \geqslant 1$, in [3] and [5] vanish. In this case, [14b], [15c], [20], and [22] reduce to the expressions for a planar surface, and ψ_{d} is described by [C2] (8). Furthermore, if $d \to 0$, the terms relating to the membrane, i.e., σ_{sl}, Y'_{Don}, and Y_{Don} vanish, and [14b], [15c], [20], and [22] reduce to the expressions for a rigid planar surface (12).

3.2. Another Approach

In an attempt to resolve the PBE for both rigid cylindrical and spherical surfaces immersed in a 1:1 electrolyte solution, Mitchell and Ninham (13) proposed a perturbation method. Although this approach appears to be different from that of Stokes (11), the rationale behind these two methods is essentially the same. Let us extend the method of Mitchell and Ninham to the present nonrigid surface and arbitrary a:b electrolyte solution. Equations [1] and [2] are recast as

$$\frac{d^2\psi}{dX^2} = \frac{g + iN}{a + b} - \frac{m}{X}\frac{d\psi}{dX}, \quad [30]$$

where i denotes the region index; $i = 0$ for the double layer, and $i = 1$ for the membrane. Integrating [30] with appropriate boundary conditions ([2a] for $i = 0$ and [2c] and [2d] for $i = 1$) yields

$$(d\psi/dX)^2 = \int_{i\psi_{\mathrm{d}}}^{\psi} \frac{2(g + iN)}{a + b}\,d\psi - \int_{i\psi_{\mathrm{d}}}^{\psi} \frac{2m}{X}\frac{d\psi}{dX}\,d\psi + i\left(\frac{d\psi}{dX}\right)^2_{\psi=\psi_{\mathrm{d}}} = \psi_{\mathrm{g}} - \int_{i\psi_{\mathrm{d}}}^{\psi} \frac{2m}{X}\frac{d\psi}{dX}\,d\psi, \quad [31]$$

where

$$\psi_{\mathrm{g}} = \left(\frac{2}{a + b}\right)^{1/2}\left[\frac{1}{b}(e^{b\psi} - 1) + \frac{1}{a}(e^{-a\psi} - 1) + iN(\psi - \psi_{\mathrm{d}})\right] + i\left(\frac{d\psi}{dX}\right)^2_{\psi=\psi_{\mathrm{d}}}. \quad [31a]$$

Substituting [31a] into the second term on the right-hand side of [31] and integrating the resultant expression yields the next order approximate solution. This procedure can be continued until a satisfactory degree of accuracy is reached. It can be shown that the result is the same as [4] and [9] up to the second order of $1/X$.

APPENDIX A

In the case where the perturbation method suggested by Stokes (11) is applied, the potential gradient $H(\psi, X)$ is defined by [3], and [1] can be written as

$$H\left(\frac{\partial H}{\partial \psi}\right)_X + \left(\frac{\partial H}{\partial X}\right)_\psi + \frac{mH}{X} - \frac{g}{a + b} = 0, \quad [\mathrm{A1}]$$

with the boundary conditions

$$H = -e\sigma_{\mathrm{dl}}/\epsilon_0\epsilon_r k_3 T\kappa \quad \text{at } X = X_0 + d \quad [\mathrm{A1a}]$$

$$H \to 0 \quad \text{as } X \to \infty. \quad [\mathrm{A1b}]$$

where σ_{dl} is the charge density at the membrane–liquid interface. Substituting [3] into [A1] and collecting terms of the same order of X leads to a set of equations in c_i. The first three of these equations are

$$c_0c'_0 = g/(a + b) \quad [\mathrm{A2a}]$$

$$c_0c'_1 + c_1c'_0 + mc_0 = 0 \quad [\mathrm{A2b}]$$

$$c_0c'_2 + c_1c'_1 + c_2c'_0 + (m - 1)c_1 = 0. \quad [\mathrm{A2c}]$$

The boundary condition [A1b] is replaced by

$$c_i \to 0 \quad \text{as } X \to \infty \quad \text{for all } i. \quad [\mathrm{A3}]$$

Solving [A2a] through [A2c] subject to [A3] gives

$$\frac{d\psi}{dX} = -\frac{2k_3}{a}\sinh(a\psi/2) - \frac{1}{X}\frac{2m}{a}\tanh(a\psi/4) + \frac{1}{X^2} \times \left[\frac{m^2\tanh^2(a\psi/4) - 4m(m-1)\ln[\cosh(a\psi/4)]}{ak_3\sinh(a\psi/2)}\right]. \quad [\mathrm{A4}]$$

APPENDIX B

Solving [7a] subject to [8] with $i = 0$, we obtain

$$d_0 = \left(\frac{2}{a + b}\right)^{1/2}\left[\frac{1}{b}(e^{b\psi} - 1) + \frac{1}{a}(e^{-a\psi} - 1) + N(\psi - \psi_{\mathrm{d}})\right] = \frac{2}{aY}(f_1/k)^{1/2}, \quad [\mathrm{B1}]$$

where Y is defined in [9d] and

$$f_1 = 1 - \frac{k}{k-2}Y^2 + \frac{2}{k-2}Y^k + 2NY^2\ln(Y/Y_d). \quad [B2]$$

Expanding the term $-md_0$ of [B1] into its Taylor series around $Y_{av} = (Y_d + Y_c)/2$, Y_d and Y_c being, respectively, the values of Y at ψ_d and at ψ_c, we obtain

$$-md_0 = \sum_{i=0}^{n_1} u_i Y^i, \quad [B3]$$

where

$$u_0 = -m[d_{0,av} - Y_{av}d'_{0,av} + (Y^2_{av}/2)d''_{0,av} - (Y^3_{av}/6)d'''_{0,av}] \quad [B3a]$$

$$u_1 = -m[d'_{0,av} - Y_{av}d''_{0,av} + (Y^2_{av}/2)d'''_{0,av}] \quad [B3b]$$

$$u_2 = -m[(1/2)d''_{0,av} - (Y_{av}/2)d'''_{0,av}] \quad [B3c]$$

$$u_3 = -m(1/6)d'''_{0,av} \quad [B3d]$$

. . .

In these expressions, $d_{0,av}$, $d'_{0,av}$, $d''_{0,av}$, and $d'''_{0,av}$ are, respectively, d_0 and its first, second, and third derivatives with respect to Y evaluated at Y_{av}.

Substituting [B1] into [7b] and solving the resultant equation subject to [8] with $i = 1$, we have

$$d_1 = \frac{2}{a(f_1^{1/2}/Y)}\left[u_0\ln\left(\frac{Y}{Y_d}\right) + \sum_{i=1}^{n_1}\frac{u_i}{i}(Y^i - Y^i_d) + \frac{2mk_3}{a} \times \left(\frac{Y_d + Y_d^{-1} - 2}{2}\right)\right]. \quad [B4]$$

The approximation below is employed in the derivation of [B4]:

$$\left(\frac{2}{a+b}\right)^{1/2}\left[\frac{1}{b}(e^{b\psi} - 1) + \frac{1}{a}(e^{-a\psi} - 1)\right]^{1/2} \simeq \frac{-2k_3}{a}\sinh(a\psi/2). \quad [B5]$$

Rewrite Eq. [7c] as

$$(d_0d_2)' = -d_1d'_1 - (m-1)d_1. \quad [B6]$$

Expand the right-hand side of [B6] into its Taylor series around Y_{av}; i.e.,

$$-d_1d'_1 - (m-1)d_1 = \sum_{i=0}^{n_2} v_i Y^i, \quad [B7]$$

where

$$v_0 = -[d_{1,av}d'_{1,av} + (m-1)d_{1,av}] + [d_{1,av}d''_{1,av} + (d'_{1,av}) + (m-1)d'_{1,av}]Y_{av} - [d_{1,av}d'''_{1,av} + 3d'_{1,av}d''_{1,av} + (m-1)d''_{1,av}]Y^2_{av} \quad [B7a]$$

$$v_1 = -[d_{1,av}d''_{1,av} + (d'_{1,av}) + (m-1)d'_{1,av}] + 2[d_{1,av}d'''_{1,av} + 3d'_{1,av}d''_{1,av} + (m-1)d''_{1,av}]Y_{av} \quad [B7b]$$

$$v_2 = -[d_{1,av}d'''_{1,av} + 3d'_{1,av}d''_{1,av} + (m-1)d''_{1,av}] \quad [B7c]$$

. . .

In these expressions, $d_{1,av}$, $d'_{1,av}$, $d''_{1,av}$, and $d'''_{1,av}$ are, respectively, d_1 and its first, second, and third derivatives with respect to Y evaluated at Y_{av}. Substituting [B7] into [B6] and solving the resultant equation subject to [8] with $i = 2$, we obtain

$$d_2 = \frac{2}{a(f_1^{1/2}/Y)}\left[v_0\ln\left(\frac{Y}{Y_d}\right) + \sum_{i=1}^{n_2}\frac{v_i}{i}(Y^i - Y^i_d) + \frac{[m(Y_d - 1)/(Y_d + 1)] - 4m(m-1)\ln[(Y_d^{1/2} - Y_d^{-1/2})/2]}{k_3(Y_d - Y_d^{-1})}\right]. \quad [B8]$$

APPENDIX C

As an initial guess for the value of Y_{Don} and Y^i_{Don}, we choose

$$Y^i_{Don} = \{\tfrac{1}{2}[(N^2 + 4)^{1/2} - N]\}^{1/2}, \quad [C1a]$$

or equivalently,

$$\psi^i_{Don} = (1/a)\sinh^{-1}(-N/2). \quad [C1b]$$

Replace the Y_{Don} in the first term on the left-hand side of [10] by [C1a], and solve the resultant expression for Y_{Don}. This step can be continued until a reasonably accurate Y_{Don} is obtained. Note that if $k = 4$ (symmetric electrolytes), [C1a] yields the exact value of Y_{Don}.

As a first approximation, [11] is solved by neglecting d_1, d_2, ... The first-order approximate solution thus obtained, $\psi_{d,1}$, is

$$\psi_{d,1} = \psi_{Don} + \frac{1}{N}\left[\frac{1}{b}(\exp(b\psi_{Don}) - 1) + \frac{1}{a}(\exp(-a\psi_{Don}) - 1)\right]. \quad [C2]$$

This is the exact solution for the case $m = 0$ (flat plate). Substituting [C2] into the second term on the left-hand side of [11], neglecting d_2, d_3, . . . , and solving the resultant equation, we obtain the second-order approximate solution $\psi_{\mathrm{d},2}$ as

$$\psi_{\mathrm{d},2} = \psi_{\mathrm{Don}} + \frac{1}{N}\left[\frac{1}{b}(\exp(b\psi_{\mathrm{Don}}) - 1) + \frac{1}{a}(\exp(-a\psi_{\mathrm{Don}}) - 1) - \frac{a+b}{2}\left(\frac{d_1(\psi_{\mathrm{Don}})_1}{X_0}\right)^2\right], \quad [\mathrm{C3}]$$

where $d_1(\psi_{\mathrm{Don}})_1$ is the value of $d_1(\psi_{\mathrm{Don}})$ with ψ_{d} replaced by $\psi_{\mathrm{d},1}$. Substituting [C3] into d_1 and d_2 in [11], neglecting d_3, d_4, . . . , and solving the resultant equation, we have the third-order approximate solution $\psi_{\mathrm{d},3}$ as

$$\psi_{\mathrm{d}} \simeq \psi_{\mathrm{d},3} = \psi_{\mathrm{Don}} + \frac{1}{N}\left\{\frac{1}{b}(\exp(b\psi_{\mathrm{Don}}) - 1) + \frac{1}{a}(\exp(-a\psi_{\mathrm{Don}}) - 1) - \frac{a+b}{2}\left[\frac{d_1(\psi_{\mathrm{Don}})_2}{X_0} + \frac{d_2(\psi_{\mathrm{Don}})_2}{X_0^2}\right]\Bigg]^2\right\}, \quad [\mathrm{C4}]$$

where $d_1(\psi_{\mathrm{Don}})_2$ and $d_2(\psi_{\mathrm{Don}})_2$ are, respectively, the values of $d_1(\psi_{\mathrm{Don}})$ and $d_2(\psi_{\mathrm{Don}})$ with ψ_{d} replaced by $\psi_{\mathrm{d},2}$.

APPENDIX D

Let us consider a differential volume δV in a membrane. Since the fixed charges are distributed homogeneously, the amount of fixed charges in δV, δM, is

$$\delta M = \begin{cases} 2\pi L Z e N_0 \kappa^{-3} X\,\delta X & \text{for a cylinder} \\ 4\pi Z e N_0 \kappa^{-3} X^2 \delta X & \text{for a sphere,} \end{cases} \quad [\mathrm{D1}]$$

where L/κ denotes the length of the cylinder. Corresponding to δV, the differential area of the membrane can be expressed by

$$\delta A = \begin{cases} 2\pi L \kappa^{-2}[X_0 + (\delta X/2)] & \text{for a cylinder} \\ 4\pi \kappa^{-2}[X_0 + (\delta X/2)]^2 & \text{for a sphere.} \end{cases} \quad [\mathrm{D2}]$$

The average density of fixed charges in a membrane, σ_{sl}, is calculated by

$$\sigma_{\mathrm{sl}} = \frac{M}{A} = \frac{ZeN_0\kappa^{-1}\int_{X_0}^{X_0+d} X^m \delta X}{\int_{X_0}^{X_0+d}[X_0 + (\delta X/2)]^m} \simeq ZeN_0 d\kappa^{-1}, \quad m = 1 \text{ or } 2, \quad [\mathrm{D3}]$$

where $m = 1$ for a cylinder and $m = 2$ for a sphere. In the derivation of this expression we assume that $(d/X_0) \ll 1$. Thus, the average density of fixed charges for cylindrical and spherical particles is the same as that for a flat particle (8).

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