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The three-dimensional problem of a charged spherical particle immersed in an ionic solution is solved asymptotically. The small parameter used is δ/a, where δ is the Debye screening distance and a the radius of the particle. The solutions to the Poisson–Boltzmann equation are obtained inside the double layer and outside the double layer. They are matched together asymptotically to obtain a solution whose error is of order δ^2/a^2 smaller than the expression kept. A uniform solution valid in all the regions is also obtained. Comparison with numerical solution to the problem, which is usually tedious, shows excellent agreement.

In this paper, we obtain an approximate analytical expression for the potential outside a spherical particle, with a fixed potential (or fixed charge) immersed in an electrolyte, in the thin double layer approximations — $\delta \ll a$, where δ is the double layer thickness and a the radius of the particle. The results agree extremely well with numerical results[1,2] up to $\delta \lesssim a$. The results are given up to zeroth and first orders in (δ/a), but the general method of matched asymptotic expansions described here can easily be extended to higher orders. The solution of Poisson–Boltzmann equation in the absence of an electric field is an essential prerequisite for studying many interesting physical phenomena such as electrophoretic mobility[1,2,4] electroviscous effects,[2,4-6] dielectric response,[7-9] a host of electrokinetic effects[10,11] electrical conductivity,[12,13] to name a few. Simple approximate solutions such as linearized solution are known to be not adequate for these calculations.[1,2]

The Poisson–Boltzmann equation can be solved exactly in one dimension[2] and two dimensions for cylindrical rods.[13] Due to its importance, this equation has received much attention. The equation for a sphere has been solved numerically.[1-3,14-16] Linearized analytical solution has been obtained by Debye–Hückel.[14] An implicit iterative solution expressing r as a function of the potential Φ has been obtained by Parlange.[17,18] Abraham-Shrauner[19] has obtained higher order solution, but it is only valid inside the double layer. Sigal and Semenikhin[20] have obtained analytical solution through a different scheme of successive approximations. The differential equation becomes very complicated at the higher approximations, and it is not clear how the higher-order solutions can be easily obtained. Our analytic result, using the method of matched asymptotic expansions,[21] is systematic, and can be extended to finding higher order solution easily. A uniformly valid solution, valid both inside and outside the double layer, and where Φ is given explicitly in terms of r is presented. The Poisson–Boltzmann equation to be solved is

$$\nabla^2 \Phi = -\frac{e}{\epsilon}(N_+ - N_-) . \tag{1}$$

Here ϵ is the dielectric constant of the electrolyte, and N_+ and N_-, the positive and negative ion density in the solution, which are related to the potential by the Boltzmann distribution

$$N_\pm = N_0 e^{\mp e\Phi/k_B T} , \tag{2}$$

N_0 being the charge density far away from the particle. Equation (1) can be rewritten in terms of a dimensionless potential $\Psi = (e/k_B T)\Phi$ as

$$\nabla^2 \Psi = \frac{1}{\delta^2} \sinh \Psi , \tag{3}$$

where $\delta^2 = \epsilon k_B T/(e^2 2N_0)$ is the screening distance. The boundary condition being $\Psi = \Psi_0$ at $r = a$, the surface of the sphere and $\Psi \to 0$ as $r \to \infty$.

Sherwood[2] claimed that the boundary layer thickness is of the order of $\delta e^{-\Psi_0/2}$, therefore a matching region does not exist when Ψ_0 is large. However, if we take the inner region to be of thickness δ, we can obtain matched asymptotic expansions[21] to the problem. Taking (δ/a) as the small parameter, and using the approximation

$$\Psi \sim \Psi^{(0)} + (\delta/a)\Psi^{(1)} + \cdots \tag{4}$$

in Eq. (3) gives

$$\frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r}\left[\Psi^{(0)} + (\delta/a)\Psi^{(1)} + \cdots\right]$$
$$= \frac{1}{\delta^2}\sinh[\Psi^{(0)} + (\delta/a)\Psi^{(1)} + \cdots] . \tag{5}$$

First consider the inner region solution. By a coordinate transformation

$$r = a + \delta x, \quad \delta x \ll a , \tag{6}$$

we can stretch and emphasize the double layer zone. Using Eq. (6) in Eq. (5) giving

$$\left(\frac{1}{\delta^2}\frac{d^2}{dx^2} + \frac{2}{(a+\delta x)\delta}\frac{d}{dx}\right)\left[\Psi_{\text{inn}}^{(0)} + \left(\frac{\delta}{a}\right)\Psi_{\text{inn}}^{(1)} + \cdots\right]$$
$$= \frac{1}{\delta^2}\sinh\left[\Psi_{\text{inn}}^{(0)} + \left(\frac{\delta}{a}\right)\Psi_{\text{inn}}^{(1)} + \cdots\right] . \tag{7}$$

Collecting terms of the same power of δ on both sides gives

$$\frac{d^2}{dx^2}\Psi_{\text{inn}}^{(0)} = \sinh \Psi_{\text{inn}}^{(0)} \tag{8}$$

in the double layer. The solution to Eq. (8) is well known[1] and is given by

$$\Psi_{\text{inn}}^{(0)}(x) = 2\ln\left(\frac{1+te^{-x}}{1-te^{-x}}\right), \quad t = \tanh(\Psi_0/4) . \tag{9}$$
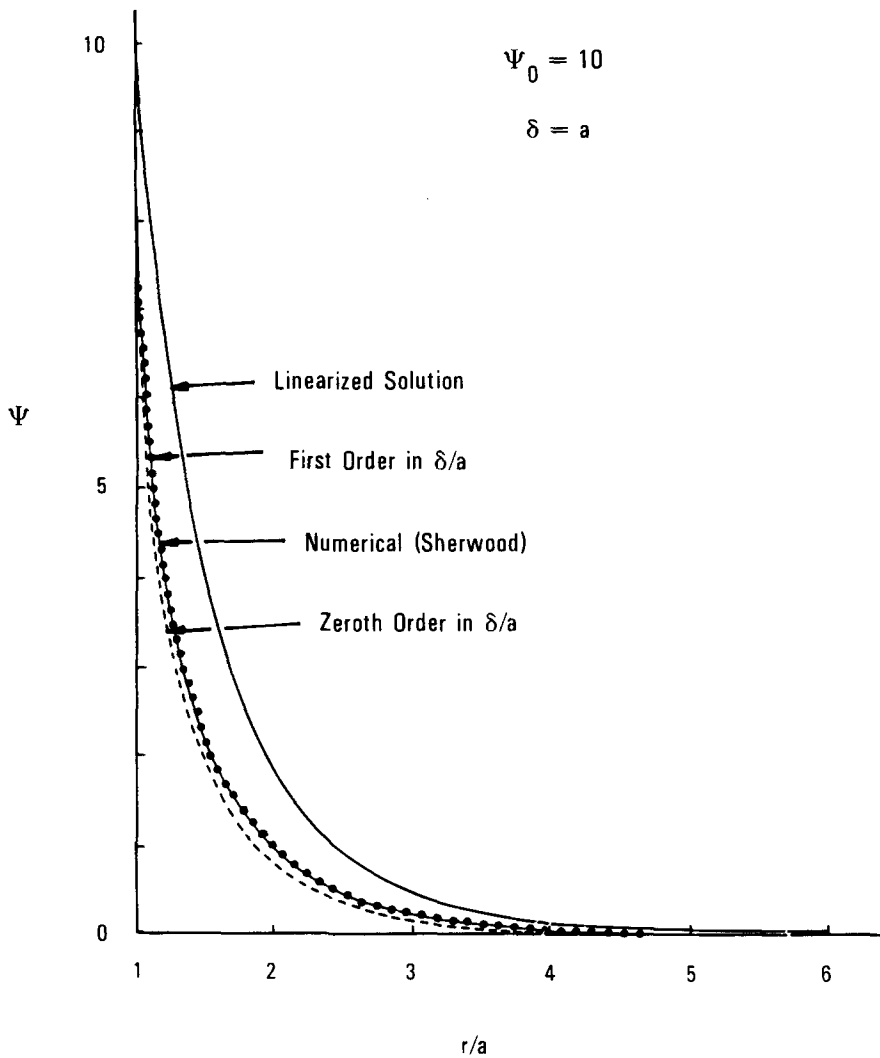
FIG. 1. Potential as a function of distance r/a (a being the particle radius) for a high zeta potential $\Psi_0 = 10$. The extreme case of $\delta = a$ is shown here. The dashed line corresponds to the zeroth order term in Eq. (16), while the dotted line corresponds to the full Eq. (16).

In going from Eq. (8) to Eq. (9), the boundary conditions that $\Psi^{(0)}$ and $\partial\Psi^{(0)}/\partial x$ tend to zero as $x \to \infty$ were used. This amounts to assuming that $\Psi^{(0)}$, $\partial\Psi^{(0)}/\partial x$ become very small when one is sufficiently far from the double layer region. One can still satisfy $\delta x/a \ll 1$ simultaneously with x large, since $\delta/a \to 0$. Next collecting terms of order $1/\delta$ in Eq. (7) gives

$$\frac{d^2}{dx^2}\Psi_{\text{inn}}^{(1)} - \cosh(\Psi_{\text{inn}}^{(0)})\Psi_{\text{inn}}^{(1)} = -2\frac{d}{dx}\Psi_{\text{inn}}^{(0)} . \tag{10}$$

Equation (10), with boundary conditions $\Psi_{\text{inn}}^{(1)} = 0$ at $x = 0$ and $x \to \infty$ has a solution.

$$\Psi_{\text{inn}}^{(1)}(x) = \frac{2t\,e^{-x}}{(1-t^2 e^{-2x})}\left[t^2(1-e^{-2x}) - 2x\right] . \tag{11}$$

Combining Eq. (9) and Eq. (11) gives

$$\Psi_{\text{inn}}(x) \sim \Psi_{\text{inn}}^{(0)} + (\delta/a)\Psi_{\text{inn}}^{(1)} = 2\ln\left(\frac{1+t\,e^{-x}}{1-t\,e^{-x}}\right)$$

$$+ \frac{\delta 2t\,e^{-x}}{a(1-t^2 e^{-2x})}\left[t^2(1-e^{-2x}) - 2x\right] . \tag{12}$$

As $x \to \infty$, Eq. (12) gives

$$\Psi_{\text{inn}} \sim 4t\,e^{-x} + (\delta/a)\,2t(t^2-2x)\,e^{-x} + O[(\delta/a)^2] . \tag{13}$$

This shows how the surface potential is screened by the charge cloud and Ψ decreases exponentially with distance. This helps us to obtain the outer solution.

Since the potential is exponentially small at large distance, we can obtain the outer solution by linearizing $\sinh\Psi \sim \Psi$,

$$\Psi_{\text{out}}(r) \sim \Psi_{\text{out}}^{(0)} + \left(\frac{\delta}{a}\right)\Psi_{\text{out}}^{(1)} = \frac{A\,e^{-(r-a)/\delta}}{r} + \frac{\delta B\,e^{-(r-a)/\delta}}{ar} . \tag{14}$$

Expressing r in terms of the inner variable $\delta x = (r-a)$, and comparing with Eq. (13) we find

$$A = 4at ,$$

$$B = 2t^3 a . \tag{15}$$

An asymptotic solution which is valid uniformly throughout the inner and the outer region can be obtained by combining Eqs. (12) and (14).[22]

$$\Psi_{\text{unif}} \sim \Psi_{\text{inn}}\left(\frac{r-a}{\delta}\right) + \Psi_{\text{out}}(r) - 4t\,e^{-(r-a)/\delta}$$

$$- \frac{2\delta t[t^2 - 2(r-a)/\delta]e^{-(r-a)/\delta}}{a} + O(\delta^2/a^2) , \tag{16}$$

where the last two terms are the limiting form of the outer and inner solutions in the matching region, i.e.,

$\lim_{r\to a}\Psi_{out} \sim \lim_{x\to\infty}\Psi_{inn}$. One can easily verify that $\lim_{r\to a}\Psi_{unit} \sim \Psi_{inn}$ and $\lim_{r/\delta\to\infty}\Psi_{unit} \sim \Psi_{out}$.

For the fixed potential case, we can obtain the excess charge near the particle by using Gauss's theorem on Eq. (1) to give

$$Q_{ex} = \epsilon \int_{S_a} \hat{r} \cdot \nabla\Phi \, ds .\tag{17}$$

Here S_a is the surface of the sphere.

This should be equal and opposite to Q_p, the charge in the particle, i.e., $Q_{ex} + Q_p = 0$, for over all charge neutrality. Using Eq. (12) in Eq. (17) gives

$$Q_{ex} = -16\pi a^2 N_0 e \delta \left[\sinh\frac{\Psi_0}{2} + \frac{2\delta \tanh(\Psi_0/4)}{a} \right] + O(\delta^3/a^3) .\tag{18}$$

Thus a negative Q_p corresponds to a negative Ψ_0. This expression agrees with the expression for charge given by Sigal and Semenikhin[20] except that we give an estimate of error in Eq. (18). Their procedure is different and their analytical solution has a form different from our Eq. (16). The method of matched asymptotics exploited here gives a control on the error. Sigal and Semenikhin's iterative scheme is not systematic. For example, when $\delta/a \ll 1$, our zeroth order solution has the correct $(1/r)e^{-(r-a)/\delta}$ form in the outer region, but theirs do not. Therefore, their zeroth order solution will compare poorly with the numerical solution, whereas our zeroth order solution compares excellently with the numerical solution in all regions even when $\delta \sim a$, as shown in Fig. 1.

Our results correspond very closely to those obtained by Sherwood.[1,2] Sherwood also has obtained Ψ_{inn} to order (δ/a). Sherwood's Eq. (2) is identical to our Eq. (9) and his first equation defining p_1 on p. 612 of Ref. 2 is identical to our Eq. (11). He also linearized the outer solution, just like us. However, he matched the inner and outer solution for the case $\Psi_0 \to \infty$, while he could have matched solutions for all Ψ_0 quite easily, as we have done here. This matching for arbitrary Ψ_0 is rather important, particularly if we compare Ψ_{unit} given by Eq. (16) with Fig. 3.1 of Ref. 1. The agreement with numerical solution is remarkably well as shown in Fig. 1. From Eq. (16) we also find $\Psi(r\to\infty) \sim \Psi_{1lm}(a/r)$ $\times \exp[-(r-a)/\delta]$, where

$$\Psi_{1lm} = 4t + 2\delta t^2/a .\tag{19}$$

Thus, at large distance the solution looks like a linear-

ized solution except that Ψ_0 has been replaced by Ψ_{1lm}. We find as $\Psi_0 \to 0$, $t \to \Psi_0/4$ giving the correct limiting form $\Psi_{1lm} \to \Psi_0$. When $\Psi_0 \to \infty$, $t \to 1$, Eq. (23) gives

$$\Psi_{1lm} = 4 + 2\delta/a ,$$

which agrees with Sherwood's result.[1,2] For small Ψ_0, Ψ_{1lm} is extremely accurate for $\delta \sim a$. For large Ψ_0, Ψ_{1lm} seems to be accurate to about 20% for $\delta \sim a$. Our result compares very well with the numerical result in the table of Ref. 18.

ACKNOWLEDGMENT

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