

# Electrical Potential Distribution around a Charged Colloidal Particle: Nonlinear Integral Equation

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**Abstract** The electrical potential distribution around a charged colloidal particle in a solution of general electrolytes is governed by the nonlinear Poisson-Boltzmann equation, which is a *differential* equation and difficult to solve analytically. In this paper we numerically calculate the electrical potential using nonlinear Qian Poisson-Boltzmann *integral* equation (PBIE). First, we introduce the PBIE derived from the physical principles for electrostatic fields and thermodynamic systems. Then the PBIE is numerically solved by means of iteration, in which the discrete potential is solely used. Finally, the accuracy of the numerical solutions proposed here is discussed. The potentials for the colloidal particles with scaled radius  $\kappa a$  of  $0.1\sqrt{2}$  and  $0.2\sqrt{2}$  are obtained in the case that scaled surface potential  $e\zeta/kT$  is equal to 1, 2, 4, and 6, respectively. The surface charge densities are also calculated to be compared with the accurate numerical solutions in 3-1 electrolyte given by Loeb *et al* (1961) and Oshima (1995). Excellent agreement is achieved. The relative errors of surface charge densities between the compared solutions are less than 1.0%.

**Key words** Electrical potential distribution, Colloidal particle, General electrolyte, Electrical double layer, Poisson-Boltzmann equation, Integral equation

## INTRODUCTION

Knowledge of electrical potential distribution is an essential basis of analyzing the electrostatic interaction of charged colloidal particles in a solution of electrolytes, such as surface charge density/surface potential relationship, stability of the dispersion, and electrokinetic effects<sup>[1,2]</sup>. The potential distribution around a charged colloidal particle is governed by nonlinear Poisson-Boltzmann equation (PBE), which is a differential equation and difficult to solve analytically. The PBE can be analytically solved only when the scaled surface potential is so small that linearized PBE can be used.

On the other hand, the nonlinear PBE can be numerically solved for whole range of scaled

surface potentials using finite difference method<sup>[3,4]</sup>, finite element method<sup>[5]</sup>, and network method<sup>[6]</sup>. Unfortunately, these numerical approaches may be get into trouble and out of work when the scaled surface potential is much larger, because the potential near the surface of the particle varies very steeply and its derivatives can not be reasonably approached. To avoid the steep variation, Strauss et al<sup>[7]</sup> proposed a transform of the potential. Bowen et al<sup>[4]</sup> then improved the transform and used it to solve numerically the PBE. However, the transform does not completely avoid the steep variation, because their numerical calculation is based on Poisson-Boltzmann differential equation (PBDE) and the derivatives of the potential can not be reasonably approximated by their differences in the case of high scaled surface potentials.

Qian et al<sup>[8,9]</sup> proposed another numerical method, called integral equation method (IEM), based on Poisson-Boltzmann integral equation (PBIE) in which the derivatives of the potential are not used. In the present paper we extend the IEM from a charged capillary to for a charged spherical colloidal particle. First, we introduce a PBIE governing the potential around the particle according to the physical principles for electrostatic fields and thermodynamic systems. Then, the PBIE is numerically solved by means of iteration, in which the discrete potential is solely used. Finally, we discuss the accuracy of the numerical solutions proposed here. The potential for particles with scaled radius  $\kappa a$  of  $0.1\sqrt{2}$  and  $0.2\sqrt{2}$  are obtained in the case that scaled surface potential  $e\zeta/kT$  is equal to 1, 2, 4, and 6, respectively. The surface charge densities are also calculated to be compared with the accurate numerical solutions in 3-1 electrolyte given by Loeb et al<sup>[3]</sup> and Oshima<sup>[10]</sup>. Excellent agreement is achieved. The relative errors of surface charge densities between the compared solutions are less than 1.0%.

## SPHERICAL POISSON-BOLTZMANN DIFFERENTIAL EQUATION

As Oshima does in paper [10], consider a spherical colloidal particle of radius  $a$  immersed in a solution of general electrolytes which is composed of  $N$  ionic mobile species of valence  $z_i$  and bulk number density  $n_i^0$  ( $i=1, 2, \dots, N$ ), where

$$\sum_{i=1}^N z_i n_i^0 = 0 \quad (1)$$

since electroneutrality holds in the bulk solution phase. In the condition of electrostatic equilibrium, the electrical potential  $\mathcal{Q}(r)$  at a distance  $r$  from the center of the particle (measured relative to the bulk solution phase, where  $\mathcal{Q}(r)=0$ ) is determined by the spherical Poisson-Boltzmann equation (PBE),

$$\frac{d^2\mathcal{Q}}{dr^2} + \frac{2}{r} \frac{d\mathcal{Q}}{dr} = - \frac{e}{\epsilon} \sum_{i=1}^N z_i n_i^0 \exp\left(-\frac{z_i e \mathcal{Q}}{kT}\right), \quad (2)$$

where  $e$  is the elementary electric charge,  $\epsilon$  is the permittivity of the solution,  $k$  is the Boltzmann constant, and  $T$  is the absolute temperature. For the most case we employ the constant surface potential condition, that is,

$$\varphi(r) = \zeta \quad \text{at } r = a \quad (3)$$

where  $\zeta$  is the surface potential ( zeta potential ) of the particle. The natural boundary conditions are also used,

$$\varphi(r) = \frac{d\varphi}{dr} = 0 \quad \text{at } r = \infty \quad (4)$$

When the scaled potential  $\Phi$ , the scaled surface potential  $\xi$ , and the scaled radius  $R$  are used, that is,

$$\Phi = \frac{e\varphi}{kT}, \quad \xi = \frac{e\zeta}{kT}, \quad R = \kappa r, \quad (5)$$

where  $\kappa$  is the Debye-Huckel parameter of the solution and is defined as

$$\kappa = \left( \frac{e^2}{kT} \sum_{i=1}^N z_i^2 n_i^0 \right)^{1/2}, \quad (6)$$

then Eqs (2)-(4) become

$$\frac{d^2\Phi}{dR^2} + \frac{2}{R} \frac{d\Phi}{dR} = - \sum_{i=1}^N z_i C_i^0 \exp(-z_i\Phi), \quad (7)$$

$$\Phi(R) = \xi \quad \text{at } R = R_s = \kappa a, \quad (8)$$

$$\Phi(R) = \frac{d\Phi}{dR} = 0 \quad \text{at } R = \infty, \quad (9)$$

where  $C_i^0 = n_i^0 / \sum_{i=1}^N z_i n_i^0$  is the relative concentration,  $R_s$  is the scaled radius of the particle, and Eq (7) is called normalized PBDE. Eqs (2)-(4) or Eqs (7)-(9) set the boundary value problem of the electrostatic potential distribution around a charged colloidal particle.

The surface charge density  $\sigma$  of the particle is given by

$$\sigma = - \epsilon \left. \frac{d\varphi}{dr} \right|_{r=a^+} = \frac{\epsilon \kappa kT}{e} I, \quad (10)$$

where

$$I = - \left. \frac{d\Phi}{dR} \right|_{R=R_s^+} \quad (11)$$

Equation (10) with Eq (11) gives the surface charge density/surface potential relationship or the  $I/\xi$  relationship for the particle.

## SPHERICAL POISSON-BOLTZMANN INTEGRAL EQUATION

Following Qian et al<sup>[8,9]</sup>, we now give a nonlinear spherical Poisson-Boltzmann integral equation (PBIE) governing the potential at the outside of a charged colloidal particle. In thermal equilibrium, the ionic number density  $n_i(r)$  of its species around the particle obeys Boltzmann distribution:

$$n_i(r) = n_i^0 \exp(-z_i e \varphi / kT). \quad (12)$$

And the charge density  $\rho(r)$  is

$$\rho(r) = \sum_{i=1}^N e z_i n_i(r). \quad (13)$$

In electrostatic equilibrium, the electric field strength  $E(r)$  at the outside of the particle is described by Gauss Theorem<sup>[11]</sup>, and we can get in SI units,

$$E(r) = \frac{q(r)}{4\pi\epsilon r^2}, \quad (14)$$

where

$$q(r) = 4\pi \int_0^r \rho(r) r^2 dr \quad (15)$$

The charge  $q(r)$  in Eq (15) is the total electric charge within the spherical surface of radius  $r$ . According to the electroneutrality in all solution space around the particle, It can be derived from Eq (15) that

$$q(r) = - 4\pi \int_r^\infty \rho(r) r^2 dr \quad (16)$$

Based on the definition of electric potential difference given by Guo<sup>[11]</sup>, the electric potential difference between potential  $\mathcal{Q}(r)$  at  $r$  and potential  $\mathcal{Q}(\infty) = 0$  at  $r = \infty$ ,

$$\mathcal{Q}(r) - \mathcal{Q}(\infty) = \int_r^\infty E(r) dr \quad (17)$$

Substituting Eqs (12)- (14) into Eq (17), we get

$$\mathcal{Q}(r) = - \frac{1}{\epsilon} \int_{i=1}^N e z_i n_i^0 \int_r^\infty \frac{dx}{x^2} \int_x^\infty y^2 \exp(- e z_i \mathcal{Q}(y)/kT) dy, \quad (18)$$

where variables  $x$  and  $y$  are auxilliary integral variables with no physical sense. Eq (18) is called spherical nonlinear PBIE. The boundary conditions connected with Eq (18) are,

$$\mathcal{Q}(a) = \zeta, \quad \mathcal{Q}(\infty) = \frac{d\mathcal{Q}}{dr} = 0. \quad (19)$$

If scaled potential  $\Phi$ , scaled zeta potential  $\xi$  and scaled radius  $R$  are used, the normalized PBIE can be obtained,

$$\Phi(R) = - \frac{1}{R} \int_{i=1}^N z_i C_i^0 \int_R^\infty \frac{dX}{X^2} \int_X^\infty Y^2 \exp(- z_i \Phi(Y)) dY, \quad (20)$$

where variables  $X$  and  $Y$  are also auxilliary integral variables with no physical sense. The boundary conditions connected with Eq (20) are

$$\Phi(R_s) = \xi, \quad \Phi(\infty) = \frac{d\Phi}{dR} = 0. \quad (21)$$

## NUMERICAL SOLUTION TO PBIE

Based on the method developed previously by Qian et al<sup>[8,9]</sup>, we first select an interval  $(R_s, R_c)$ .  $R_c$  is a scaled radius as reference for numerical recursive procedure employed below. The reference radius  $R_c$  is so selected that we can use Debye-Huckel approximation to express the potential when scaled radius  $R$  is larger than  $R_c$ , that is,

$$\Phi(R) \approx \frac{1}{R} \exp(- R), \quad \text{when } R > R_c, \quad (22)$$

and

$$\int_{R_c}^{\infty} \Phi(R) R^2 dR = R_c (1 + R_c) \Phi(R_c). \quad (23)$$

Divide the interval  $(R_s, R_c)$  into  $M$  subintervals  $(R_{j-1}, R_j)$ ,  $j = 1, 2, \dots, M$ , and there are  $M + 1$  nodes:  $R_s = R_0 < R_1 < \dots < R_M = R_c$  in the interval  $(R_s, R_c)$ . Discretize Eq (20) and get a discrete spherical PBIE,

$$\Phi_{m-1} = \Phi_m - \frac{R_m}{R_{m-1}} \frac{dX}{X^2} \sum_{j=m}^M \int_{R_{j-1}}^{R_j} dY Y^2 \int_{i=1}^N z_i C_i^0 \exp(- z_i \Phi(Y)), \quad (24)$$

where  $\Phi_m = \Phi(R_m)$ ,  $m = 0, 1, \dots, M$ ,  $\Delta_j = R_j - R_{j-1}$  is the length of subinterval  $(R_{j-1}, R_j)$ ,  $j =$

1, 2, ..., M, which may be either constant or variable. The integration in subinterval ( $R_{j-1}$ ,  $R_j$ ) or ( $R_{m-1}$ ,  $R_m$ ) is linearly approximated.

According to Eq. (21),  $\Phi$  should be equal to  $\xi$ , and it can be derived from Eqs. (22~23) that

$$\Phi_{M-1} = \Phi_M \left(1 - \Delta_M \frac{1+R_c}{R_c}\right). \quad (25)$$

Using Eq. (24), the value of  $\Phi$  at each node can be recursively calculated from the reference point  $R_c$  to the surface  $R_s$  of the particle.

According to  $\Phi$ 's property of monotonously increasing or decreasing, the updated starting value  $\Phi_M^{K+1}$  in (K+1)th iteration is achieved by setting

$$\Phi_M^{K+1} = (\Phi_{M,\max}^{K+1} + \Phi_{M,\min}^{K+1}) / 2, \quad (26)$$

where if  $\Phi_M^K > \xi$ , then

$$\Phi_{M,\max}^{K+1} = \Phi_M^K, \quad \Phi_{M,\min}^{K+1} = \Phi_{M,\min}^K, \quad (27)$$

and if  $\Phi_M^K < \xi$ , then

$$\Phi_{M,\max}^{K+1} = \Phi_{M,\max}^K, \quad \Phi_{M,\min}^{K+1} = \Phi_M^K. \quad (28)$$

In the first iteration we take

$$\Phi_{M,\max}^1 = \xi, \quad \Phi_{M,\min}^1 = 0, \quad (29)$$

where  $\Phi_M^K$  is the Kth starting value. The iterative process is continued until the relative error between  $\Phi_M^K$  and the correct boundary value  $\xi$  meets the requirement.

The above updating method of starting value makes the iterative process be of faster convergence than that proposed by Qian *et al* in paper<sup>[8,9]</sup>.

## EXAM PLES

For comparison of the present results with the exact numerical values by Loeb *et al* (Table 3 in Ref. (3)) and accurate analytic approximation by Oshima (Table 1 in Ref. (10)), we take 3-1 electrolytes of concentration  $n$  as an example. In our numerical computation of  $\Phi$ , let subinterval length  $\Delta$  constant and equal to  $(R_c - R_s)/5000$ , desired relative error of the potential at  $R_s$  less than 0.001%, that is  $|\Phi_M^K - \xi|/\xi < 0.001\%$ .

Figure 1 illustrates our numerical results of  $\Phi$  from Eq. (24), provided that scaled radius  $R_s = 0.1\sqrt{2}$  and scaled potential  $\xi = 1, 2, 4$ , and 6, respectively. Figure 2 illustrates our solutions of  $\Phi$  from Eq. (24), in the case that scaled radius  $R_s = 0.2\sqrt{2}$  and scaled potential  $\xi = 1, 2, 4$ , and 6, respectively. These results show us what the electrical potential near the outer surface of a charged colloidal particle immersed in a solution of general electrolytes looks really like.

## ACCURACY OF SOLUTIONS

For testing the accuracy of our numerical solutions, we use the existed results provided by Loeb *et al*<sup>[3]</sup> and Oshima<sup>[10]</sup>, and calculate the surface charge density/surface potential relationship shown in Eqs. (10) and (11) using finite difference method. That is

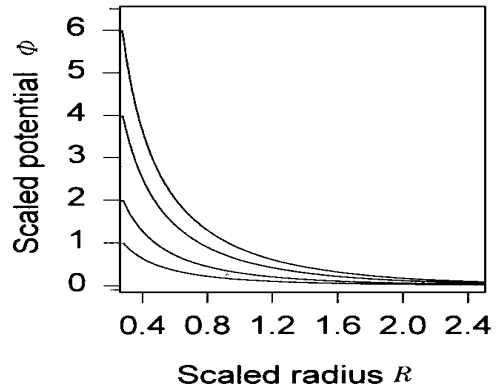
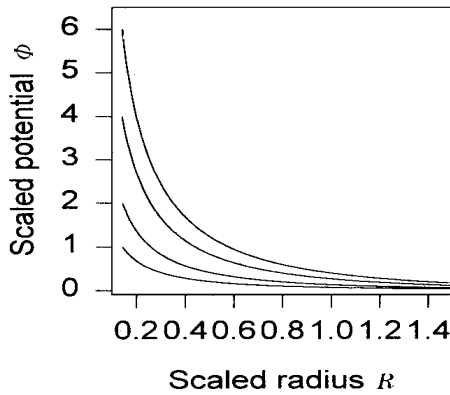


Fig 1 Numerical solutions of potential for a charged particle with radius  $R_s$  of 0.1

Fig 2 Numerical solutions of potential for a charged particle with radius  $R_s$  of 0.2

$$\left. \frac{d\Phi}{dR} \right|_{R_s} = \frac{\Phi_s - \Phi_0}{\Delta} \sqrt{2} \text{ in 3-1 electrolyte solution} \quad (30)$$

In Table 1 we show I calculated with Eqs (11, 30) as a function of scaled radius  $R_s$  and scaled surface potential  $\xi$  for 3-1 electrolytes of concentration  $n$ . The agreement between the compared solutions is excellent. The relative error between our results and the Loeb's is less than 1% for  $R_s = 0.1\sqrt{2}$ , which is better than that of Oshima<sup>[10]</sup>.

But we have to say that our results is affected by the position of the reference point  $R_s$  as shown in Table 1. From our experiments the reference point should be so selected that the scaled potential  $\Phi_s$  at  $R_c$  is less than 0.02 so as to ensure that  $\exp(\Phi)$  can be well approximated by the  $(1 + \Phi)$ .

Tab 1 The accuracy comparison of numerical solution for surface charge density of a charged colloidal particle

Scaled Radius $R_s$	Scaled Potential $\xi$	Charge Density $\sqrt{2} I(\text{LOW})$	Charge Density $\sqrt{2} I(\text{Osh 2})$	Charge Density $\sqrt{2} I(\text{Eq (27)})$	Reference Point $R_c$
$0.1\sqrt{2}$	1	11.291	11.383	11.291	$0.38\sqrt{2}$
	2	22.514	22.550	22.520	$0.45\sqrt{2}$
	4	45.465	44.292(2.6)	45.470	$0.53\sqrt{2}$
	6	71.455	68.526(4.1)	71.452	$0.53\sqrt{2}$
$0.2\sqrt{2}$	1	6.262	6.292	6.274	$0.60\sqrt{2}$
	2	12.472	12.479	12.487	$0.75\sqrt{2}$
	4	25.762	25.391(1.4)	25.780	$0.85\sqrt{2}$
	6	43.656	42.925(1.7)	43.648	$0.80\sqrt{2}$

\*  $I(\text{LOW})$  is exact numerical values of Loeb et al(3),  $I(\text{Osh 2})$  calculated with second-order relationship Eq (26) by Oshima (10), and  $I(\text{Eq (27)})$  in the present paper, respectively. The relative error,  $\epsilon = ($

$I/I(\text{LOW}) \times 100\%$ , is indicated in parentheses if more than 1%

## CONCLUSIONS

Even for small scaled radius and large scaled surface potentials the method proposed in this paper can give an accurate numerical solution of the nonlinear PBE around a charged colloidal particle in general electrolyte solution by means of the nonlinear Poisson-Boltzmann *integral* equation.

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# 带电胶体粒子的电势分布: 非线性积分方程

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**摘要** 多电解质溶液中带电胶体粒子的电势分布由球形 Poisson-Boltzmann 方程 (PBE) 描述。PBE 是一个非线性的微分方程, 且难以求得解析解。本文采用非线性 P-B 积分方程, 计算电势分布的数值解。首先, 根据静电场和热力学系统中的物理定理, 导出描述电势分布的 P-B 积分方程 (PBIE); 其次, 用迭代方法求 PBIE 的数值解。最后, 计算了在 3-1 型电解液中无量纲半径  $\kappa a$  分别为  $0.1\sqrt{2}$  和  $0.2\sqrt{2}$ , 无量纲表面电势  $\xi$  分别为 1, 2, 4, 6 时球形胶体粒子外部的电势值。为了检验数值解的精度, 计算了表面电荷密度, 并与 Loeb (1961) 和 Oshima (1995) 等人的结果比较, 本文结果的相对误差小于 1%, 优于 Oshima 的结果。

**关键词** 电势分布, 胶体粒子, 双电层, Poisson-Boltzmann 方程, 积分方程, 数值解