



# Analytical solution of Poisson–Boltzmann equation for interacting plates of arbitrary potentials and same sign

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## ABSTRACT

Efficient calculation of electrostatic interactions in colloidal systems is becoming more important with the advent of such probing techniques as atomic force microscopy. Such practice requires solving the nonlinear Poisson–Boltzmann equation (PBE). Unfortunately, explicit analytical solutions are available only for the weakly charged surfaces. Analysis of arbitrarily charged surfaces is possible only through cumbersome numerical computations. A compact analytical solution of the one-dimensional PBE is presented for two plates interacting in symmetrical electrolytes. The plates can have arbitrary surface potentials at infinite separation as long they have the same sign. Such a condition covers a majority of the colloidal systems encountered. The solution leads to a simple relationship which permits determination of surface potentials, surface charge densities, and electrostatic pressures as a function of plate separation  $H$  for different charging scenarios. An analytical expression is also presented for the potential profile between the plates for a given separation. Comparison of these potential profiles with those obtained by numerical analysis shows the validity of the proposed solution.

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## 1. Introduction

The long-range electrostatic interactions between colloidal surfaces play an important role in numerous physicochemical systems in mineral, ceramics, environmental, and biological sciences. Accurate analysis of this interaction requires solving the one-dimensional nonlinear Poisson–Boltzmann equation (PBE) to determine the potential profile  $\psi(x)$  within the electrical double layer (EDL) as a function of distance  $x$  from the interacting surfaces. Though explicit relations have been developed for the potential profile  $\psi(x)$  in the vicinity of a single plate [1,2], obtaining analytical solutions for two interacting plates is only possible for the linearized versions of the PBE for weakly charged systems [3–6], and analysis of highly charged asymmetrical surfaces is only possible by the use of unwieldy complex elliptic integrals or numerical methods [7–10].

In this paper, an analytical solution of the one-dimensional nonlinear PBE is developed for two plates of arbitrary surface potentials interacting in symmetrical electrolyte solutions with the condition that potentials at infinite separation have the same sign (i.e.,  $\psi_{1\infty} \geq \psi_{2\infty} \geq 0$  or  $\psi_{1\infty} \leq \psi_{2\infty} \leq 0$ ). A majority of physicochemical systems falls within these boundary conditions. The solution yields a compact analytical expression for the potential profile  $\psi(x)$  within EDL and also allows calculation of surface potentials, surface charge densities, and electrostatic pressures as a function

of plate separation for different charging scenarios such as constant-potential and constant-charge surfaces without any need for tedious computational techniques.

## 2. Background

The one-dimensional Poisson equation relates the solution charge density  $\rho(x)$  to the potential  $\psi(x)$  within the double layer between two surfaces in electrolyte solutions:

$$\rho(x) = -\varepsilon\varepsilon_0 \frac{d^2\psi(x)}{dx^2} \quad (1)$$

The solution charge density follows a Boltzmann-type distribution of the concentration of the ions in the EDL:

$$\rho(x) = \sum_i z_i F C_{0,i} e^{\frac{z_i F \psi(x)}{RT}} \quad (2)$$

Combining Eqs. (1) and (2), assuming a  $z:z$  symmetrical electrolyte, and using dimensionless quantities  $Y = zF\psi(x)/RT$  and  $X = \kappa x$  such that  $\kappa^2 = \frac{2z^2 F^2 C_0}{\varepsilon\varepsilon_0 RT}$  give the PBE:

$$\frac{d^2 Y}{dX^2} = \sinh Y \quad (3)$$

This nonlinear differential equation in one dimension is an expression of how the potential  $Y$  varies with distance  $X$  between two plates separated by a gap  $H$  (Fig. 1). Though it is the basis of any quantitative study on the interactions between two such surfaces, Eq. (3) does not lend itself to a simple analytical solution.

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**Nomenclature**

$C_0$	electrolyte concentration in the solution	$S_2$	dimensionless surface charge density on Plate 2 at separation $H$ ; $S_2^2 = \sigma_2^2 / 2\epsilon\epsilon_0 RTC_0$
$\epsilon$	relative permittivity of water (78.5)	$S_{1\infty}$	dimensionless surface charge density on Plate 1 at infinite separation; $S_{1\infty}^2 = 2 \cosh Y_{1\infty} - 2$
$\epsilon_0$	permittivity of vacuum ( $8.854 \times 10^{-12} \text{ C}^2/\text{J m}$ )	$S_{2\infty}$	dimensionless surface charge density on Plate 2 at infinite separation; $S_{2\infty}^2 = 2 \cosh Y_{2\infty} - 2$
$\phi$	integration constant; varies with plate separation $H$ ; $\phi = S_1^2 - 2 \cosh(Y_1) = S_2^2 - 2 \cosh(Y_2)$	$T$	absolute temperature (K)
$F$	Faraday constant ( $9.64845 \times 10^4 \text{ C/mol}$ )	$x$	distance into the solution from Plate 1 located at $x = 0$ (m)
$F_{os}$	osmotic component of the force acting on the plates ( $\text{N/m}^3$ )	$X$	dimensionless distance into solution from Plate 1 located at $X = 0$ ; $X = \kappa x$
$F_{el}$	electrostatic (Maxwell) component of the force acting on the plates ( $\text{N/m}^3$ )	$X_{1,2}$	dimensionless locations $X_1$ and $X_2$ in the diffuse layer with potential $Y$
$p_{os}$	osmotic component of the overall pressure between plates ( $\text{N/m}^2$ )	$X_m$	the distance of the point where the $Y = Y_m$ from Plate 1
$p$	overall pressure between plates ( $\text{N/m}^2$ )	$X'_m$	the distance of the point where the $Y = Y_m$ from Plate 2
$P$	overall dimensionless electrostatic pressure between plates; $P = p/2RTC_0$	$\psi(x)$	potential in solution at a point $X$ between the plates (V)
$h$	distance between plates (m)	$\psi_1$	surface potential on Plate 1 at separation $h$ (V)
$H$	dimensionless distance between plates; $H = \kappa h$	$\psi_2$	surface potential on Plate 2 at separation $h$ (V)
$\kappa$	reciprocal thickness of the double layer or Debye-Hückel parameter ( $\text{m}^{-1}$ )	$\psi_{1\infty}$	surface potential on Plate 1 at infinite separation (V)
$R$	gas constant ( $8.31441 \text{ J/mol K}$ )	$\psi_{2\infty}$	surface potential on Plate 2 at infinite separation (V)
$\lambda(a, \phi)$	a function related to a specific length between plates $\lambda(a, \phi) = \int_0^1 \frac{a}{\sqrt{u(a^2 u - \phi)^2 - 4u}} du$	$Y$	dimensionless potential in solution at a point $X$ between the plates
$\rho(x)$	charge density in solution at a point $x$ between the plates ( $\text{C/m}^3$ )	$Y_1$	dimensionless surface potential on Plate 1 at separation $H$ ; $Y_1 = zF\psi_1/RT$
$\sigma_1$	surface charge density on first plate at separation $h$ ( $\text{C/m}^2$ )	$Y_2$	dimensionless surface potential on Plate 2 at separation $H$ ; $Y_2 = zF\psi_2/RT$
$\sigma_2$	surface charge density on second plate at separation $h$ ( $\text{C/m}^2$ )	$Y_{1\infty}$	dimensionless surface potential on Plate 1 at infinite separation; $Y_{1\infty} = zF\psi_{1\infty}/RT$
$S_1$	dimensionless surface charge density on Plate 1 at separation $H$ ; $S_1^2 = \sigma_1^2 / 2\epsilon\epsilon_0 RTC_0$	$Y_{2\infty}$	dimensionless surface potential on Plate 2 at infinite separation; $Y_{2\infty} = zF\psi_{2\infty}/RT$
		$Y_m$	real or imaginary potential at point $X_m$ where $dY/dX = 0$
		$z$	valence of symmetrical electrolyte

Recognizing that  $\frac{d^2 Y}{dX^2} = \frac{1}{2} \frac{1}{dY} \left(\frac{dY}{dX}\right)^2$ , the first integration yields

$$\left(\frac{dY}{dX}\right)^2 = \text{sign}(Y)(2 \cosh Y + \phi) \tag{4}$$

Eq. (4) is valid for surfaces with potentials of any magnitude and sign interacting through symmetrical electrolyte solutions. The first integration constant  $\phi$  varies as  $H$  changes. The  $\text{sign}(Y)$  takes into account that integral of  $\sinh(-Y) = -\cosh Y$ .

The charge density,  $\sigma$ , on any one of the plates is equal in magnitude but opposite in sign to the net excess charge in solution:

$$\sigma = - \int_0^\infty \rho(x) dx \tag{5}$$

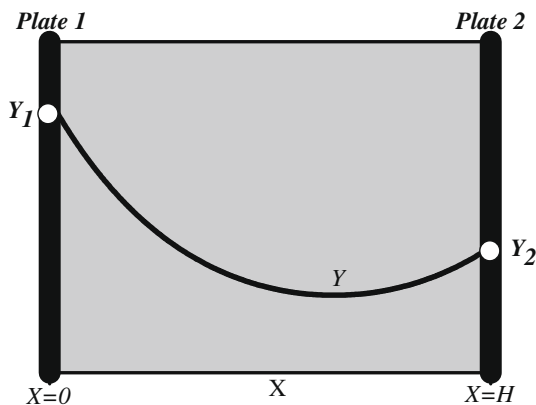


Fig. 1. Change of potential  $Y$  as a function of  $X$  between two plates.

Combining with the Poisson equation gives

$$\sigma = \epsilon\epsilon_0 \int_0^\infty \frac{d^2 \psi(x)}{dx^2} dx \tag{6}$$

Integrating once, applying the boundary conditions in Fig. 1, and expressing in terms of dimensionless quantities yield

$$S_1 = \left. \frac{dY}{dX} \right|_{X=0} = \frac{\sigma_1}{\sqrt{2\epsilon\epsilon_0 RTC_0}} \tag{7}$$

$$S_2 = \left. \frac{dY}{dX} \right|_{X=H} = \frac{\sigma_2}{\sqrt{2\epsilon\epsilon_0 RTC_0}}$$

Combining these definitions with Eq. (4) and evaluating at infinite separation where  $dY/dX = 0$  and  $Y = 0$  is satisfied for each plate demonstrate that  $\phi = -2$  when the plates are not interacting (at infinite separation). Since the potentials and charge densities on the plates satisfy  $Y_1 = Y_{1\infty}$ ,  $Y_2 = Y_{2\infty}$ ,  $S_1 = S_{1\infty}$ , and  $S_2 = S_{2\infty}$  under such conditions, it can be seen from Eqs. (4) and (7) that

$$S_{1\infty}^2 = 2 \cosh Y_{1\infty} - 2 \tag{8}$$

$$S_{2\infty}^2 = 2 \cosh Y_{2\infty} - 2$$

The surface potentials or charge densities at infinite separation can be estimated experimentally using such techniques as zeta potential measurements or colloidal titration procedures.

Evaluation of Eq. (4) on the solid/solution interface on both plates ( $X = 0$  and  $X = H$ ) shows that a general relationship can be obtained for the first integration constant  $\phi$  in terms of surface potentials and surface charge densities:

$$\phi = S_1^2 - 2 \cosh Y_1 = S_2^2 - 2 \cosh Y_2 \quad (9)$$

Note that Eq. (9) holds at all separations but the magnitude of  $\phi$  will be different for different plate separations.

Though  $Y_1$ ,  $Y_2$ ,  $S_1$ , and  $S_2$  have specific values at a given plate separation, they will change in relation to each other as  $H$  changes depending on the charging mechanism of the surfaces. For example, for constant-potential surfaces  $Y_1$  and  $Y_2$  will be equal to the surface potentials at infinite separation ( $Y_{1\infty}$  and  $Y_{2\infty}$ ) for all  $H$  whereas  $S_1$  and  $S_2$  must adjust as the planes approach. Conversely,  $S_1$  and  $S_2$  will always be equal to the surface charge densities at infinite separation ( $S_{1\infty}$  and  $S_{2\infty}$ ) for constant-charge surfaces while  $Y_1$  and  $Y_2$  will have to vary during the approach.

Charging of the surfaces leads to a pressure force experienced by the interacting plates as they approach each other. The analysis of this force has been done by Werwey and Overbeek and was shown to be due to osmotic and electrostatic effects [11]. The osmotic pressure force acting on a volume element of liquid (per unit volume) along the  $x$ -axis can be given as

$$F_{os} = -\frac{dp_{os}}{dx} \quad (10)$$

If the volume element is within a potential field, it will also experience an electrostatic force called the Maxwell stress. The  $x$ -component of this force is equal to

$$F_{el} = -\rho(x) \left( \frac{d\psi}{dx} \right) \quad (11)$$

At equilibrium, overall force balance on the volume element along the  $x$ -direction will require that

$$\frac{dp_{os}}{dx} + \rho(x) \left( \frac{d\psi}{dx} \right) = 0 \quad (12)$$

Substituting  $\rho(x)$  from Eq. (1) gives

$$\frac{dp_{os}}{dx} - \varepsilon\varepsilon_0 \left( \frac{d^2\psi(x)}{dx^2} \right) \left( \frac{d\psi}{dx} \right) = 0 \quad (13)$$

Recognizing that  $\left( \frac{d^2\psi}{dx^2} \right) \left( \frac{d\psi}{dx} \right) = \frac{1}{2} \frac{d}{dx} \left( \frac{d\psi}{dx} \right)^2$  yields

$$\frac{dp_{os}}{dx} - \frac{\varepsilon\varepsilon_0}{2} \frac{d}{dx} \left( \frac{d\psi}{dx} \right)^2 = 0 \quad (14)$$

which gives

$$p_{os} - \frac{\varepsilon\varepsilon_0}{2} \left( \frac{d\psi}{dx} \right)^2 = \text{constant} = p \quad (15)$$

It can be seen from Eq. (15) that the difference between osmotic pressure and the Maxwell stress is always equal to a constant pressure at a given separation of the plates.

The osmotic pressure component can be evaluated further by rewriting Eq. (12) such that

$$dp_{os} + \rho(x)d\psi = 0 \quad (16)$$

If  $\rho(x)$  is substituted using Eq. (2) for a  $z:z$  electrolyte, the resulting expression is in the form:

$$dp_{os} = -z_i F C_0 \left( e^{-\frac{zF\psi(x)}{RT}} - e^{\frac{zF\psi(x)}{RT}} \right) d\psi \quad (17)$$

$$dp_{os} = 2z_i F C_0 \sinh \left( \frac{zF\psi(x)}{RT} \right) d\psi \quad (18)$$

The excess osmotic pressure between the plates can be found by setting the osmotic pressure in the bulk liquid (where there are no electrostatic effects;  $\psi = 0$ ) to zero and integrating Eq. (18) between a point in bulk and any point between the plates with pressure  $p_{os}$  and potential  $\psi(x)$ :

$$p_{os} = 2RTC_0 \left[ \cosh \left( \frac{zF\psi(x)}{RT} \right) - 1 \right] \quad (19)$$

Combining Eqs. (15) and (19) gives

$$p = 2RTC_0 \left[ \cosh \left( \frac{zF\psi(x)}{RT} \right) - 1 \right] - \frac{\varepsilon\varepsilon_0}{2} \left( \frac{d\psi(x)}{dx} \right)^2 \quad (20a)$$

In terms of dimensionless quantities, it becomes

$$P = \frac{p}{2RTC_0} = [\cosh Y - 1] - 0.5 \left( \frac{dY}{dX} \right)^2 \quad (20b)$$

Eq. (20) gives the net pressure force between the two plates as a function distance from each plate. Since the two pressures must balance each other, the net pressure between the two plates must always be equal to a constant value,  $P$  for a given plate separation  $H$ .

Since the pressure will be constant at any point within the liquid separating the plates, its evaluation at one of the plates is sufficient. Doing so for Plate 2 and expressing in terms of dimensionless quantities gives the magnitude of the double layer pressure at a given separation of the plates:

$$P = [\cosh Y_2 - 1] - \frac{S_2^2}{2} \quad (21)$$

It should be noted that the pressure value obtained from Eq. (21) is meaningful only if it is paired to the distance  $H$  between the two plates.

Based on this background, a solution of the nonlinear PBE will be developed in the following paragraphs for two flat plates which carry arbitrary surface potentials at infinite separation. The plates are assumed to be interacting in symmetrical electrolyte solutions and to carry potentials of the same sign at infinite separation. It will be shown that this solution yields compact analytical expressions which explicitly relate:

- (i) the surface potentials and surface charge densities to the distance between the two plates; this information can then be directly used to obtain the electrostatic pressure at each separation;
- (ii) the potential  $Y$  to location  $X$  within the EDL for any plate separation  $H$ .

### 3. Analytical solution of the PBE for plates of arbitrary potentials and same sign

For the solution which will be developed in this paper, the double layer convention presented in Fig. 1 will be used. The coordinate system is selected such that the first surface (Plate 1) has an arbitrary potential  $Y_1$  and located at  $X=0$ . The second surface (Plate 2) has a potential  $Y_2$  and situated at  $X=H$ . The only condition employed on the potentials is that they have the same sign at infinite separation, that is,  $Y_{1\infty} \geq Y_{2\infty} \geq 0$ . Such a condition has the practical outcome that the  $\text{sign}(Y)$  in Eq. (4) can be dropped. Note that reversing the signs on both surfaces ( $Y_{1\infty} \leq Y_{2\infty} \leq 0$ ) simultaneously or switching the positions of the plates ( $Y_2$  is at  $X=0$  and  $Y_1$  is at  $X=H$ ) does not make a difference in the analysis.

Then, one can write the inverse of Eq. (4) as

$$\left( \frac{dX}{dY} \right)^2 = \frac{1}{2 \cosh Y + \phi} \quad (22)$$

By a substitution of  $\varphi = \sqrt{2 \cosh Y + \phi}$ , the above equation can be transformed to give

$$\left( \frac{dX}{d\varphi} \right)^2 = \frac{2}{(\varphi^2 - \phi)^2 - 4} \quad (23)$$

Integration of Eq. (23) yields a solution in terms of elliptic functions of the first kind, *Elliptic*<sub>F1</sub>, as

$$X = \Phi \pm 2 \sqrt{\frac{(2 + \phi) \left(1 - \frac{\phi^2}{\phi + 2}\right) \left(1 - \frac{\phi^2}{\phi - 2}\right)}{(\phi^2 - \phi)^2 - 4}} \text{Elliptic}_{F1} \left( \sin^{-1} \sqrt{\frac{\phi^2}{\phi + 2}; \frac{\phi + 2}{\phi - 2}} \right) \quad (24)$$

The second integration constant  $\Phi$  is related to some specific distance in the double layer and varies with  $H$ . The plus/minus sign which is due to the square term on the left-hand side of Eq. (23) has an important physical meaning as it will be clear shortly.

Assigning  $\frac{\phi^2}{\phi + 2} = \vartheta_1$  and  $\frac{\phi^2}{\phi - 2} = \vartheta_2$  and simplifying, Eq. (24) can be reduced to

$$X = \Phi \pm 2 \sqrt{\frac{v_2}{\phi + 2} \frac{1}{\sqrt{v_1}}} \text{Elliptic}_{F1} \left( \sin^{-1} \sqrt{v_1}; \frac{v_2}{v_1} \right) \quad (25)$$

Appell functions are a class of generalized hypergeometric functions which appear in many areas of science. Among these functions, Appell hypergeometric function of the first kind, *Appell*<sub>F1</sub>, is employed in evaluation of integrals and solution of partial differential equations. In its general form, *Appell*<sub>F1</sub> can be expressed in double integral form such that

$$\text{Appell}_{F1}(\alpha; \beta_1, \beta_2, \gamma; \vartheta_1, \vartheta_2) = \frac{\Gamma(\gamma)}{\Gamma(\beta_1)\Gamma(\beta_2)\Gamma(\gamma - \beta_1 - \beta_2)} \times \int_0^1 \int_0^{1-v} \frac{u^{\beta_1-1} v^{\beta_2-1} (1-u-v)^{\gamma-\beta_1-\beta_2-1}}{(1-u\vartheta_1 - v\vartheta_2)^{-\alpha}} du dv \quad (26)$$

where  $\Gamma(a)$  is the gamma function of argument  $a$ . For  $R(\alpha) > 0$  and  $R(\gamma - \alpha) > 0$ , *Appell*<sub>F1</sub> is in the real axis and can be expressed in terms of a simpler single integral form as [12]

$$\text{Appell}_{F1}(\alpha; \beta_1, \beta_2, \gamma; \vartheta_1, \vartheta_2) = \frac{\Gamma(\gamma)}{\Gamma(\alpha)\Gamma(\gamma - \alpha)} \times \int_0^1 \frac{u^{\alpha-1} (1-u)^{\gamma-\alpha-1}}{(1-u\vartheta_1)^{\beta_1} (1-u\vartheta_2)^{\beta_2}} du \quad (27)$$

Moreover, for  $\alpha = 0.5$ ,  $\beta_1 = 0.5$ ,  $\beta_2 = 0.5$ , and  $\gamma = 1.5$ , *Appell*<sub>F1</sub> has an equivalent counterpart in terms of *Elliptic*<sub>F1</sub> such that [13]

$$\text{Appell}_{F1}(0.5; 0.5, 0.5, 1.5; v_1, v_2) = \frac{1}{\sqrt{v_1}} \text{Elliptic}_{F1} \left( \sin^{-1} \sqrt{v_1}; \frac{v_2}{v_1} \right) \quad (28)$$

Then, combining Eqs. (25) and (28) gives

$$X = \Phi \pm 2 \sqrt{\frac{v_2}{\phi + 2}} \text{Appell}_{F1}(0.5; 0.5, 0.5, 1.5; v_1, v_2) \quad (29)$$

and applying the equality given in Eq. (27) yields:

$$X = \Phi \pm \sqrt{\frac{v_2}{\phi + 2}} \int_0^1 \frac{u^{-0.5}}{(1-u\vartheta_1)^{0.5} (1-u\vartheta_2)^{0.5}} du \quad (30)$$

Eq. (30) can be further simplified to

$$X = \Phi \pm \lambda(\varphi, \phi) \quad (31)$$

where

$$\lambda(\varphi, \phi) = \int_0^1 \frac{\varphi}{\sqrt{u(\varphi^2 u - \phi)^2 - 4u}} du \quad (32)$$

The function  $\lambda(\varphi, \phi)$  corresponds to some characteristic length between the interacting plates. It is a summation only for the parameter  $u$  within real limits  $0 \leq u \leq 1$  and can be evaluated easily as a built-in function. All the commercial mathematical software in the market (such as MathCad, Matlab, and Mathematica) or even a general scientific calculator with numerical integration

capability can handle the integral in Eq. (32) easily. Since it represents physical distance,  $\lambda(\varphi, \phi)$  should be treated as a real number, omitting the imaginary parts of any complex numbers which may arise due to the presence of square root term.

Eq. (31) has physical significance only between the two plates (i.e.,  $0 \leq X \leq H$ , where  $Y(0) = Y_1$  and  $Y(H) = Y_2$ ). However, it is mathematically valid at a wider interval  $0 \leq X \leq b$  such that  $b > H$  with  $Y(b) > Y_2$ . Then, there always exists a point  $X_m$  on the  $x$ -axis where the potential profile has a minimum  $Y = Y_m$ . For example,  $X_m$  will always be placed between 0 and  $H$  for symmetrical plates or at large separations (see Fig. 2a), but it may lay beyond  $H$  for highly asymmetrical plates or at very close separations (see Fig. 2b).

Evaluating Eq. (31) on Plate 1 ( $X=0$ ,  $S_1 = -dY/dX$  and  $Y = Y_1$ ) gives the value of  $X_m$ :

$$X_m = \int_0^1 \frac{S_1}{\sqrt{u(S_1^2 u - \phi)^2 - 4u}} du = \lambda(S_1, \phi) \quad (33)$$

Similarly, when evaluated on Plate 2 ( $X=H$ ,  $S_2 = dY/dX$  and  $Y = Y_2$ ), Eq. (31) gives

$$X'_m = \int_0^1 \frac{S_2}{\sqrt{u(S_2^2 u - \phi)^2 - 4u}} du = \lambda(S_2, \phi) \quad (34)$$

which leads to

$$H = X_m + X'_m \quad (35)$$

$$H = \lambda(S_1, \phi) + \lambda(S_2, \phi)$$

The term  $X'_m$  is simply the distance between  $X_m$  and Plate 2 (see Fig. 2). It can be seen from the figure that  $X_m > 0$  always whereas  $X'_m < 0$  when  $Y_m$  develops beyond Plate 2. For identical plates where  $Y_1 = Y_2$ , the potential profile  $Y$  is symmetrical on both sides of  $X_m$  and Eq. (31) simplifies to  $H = 2X_m = 2\lambda(S_1, \phi)$ .

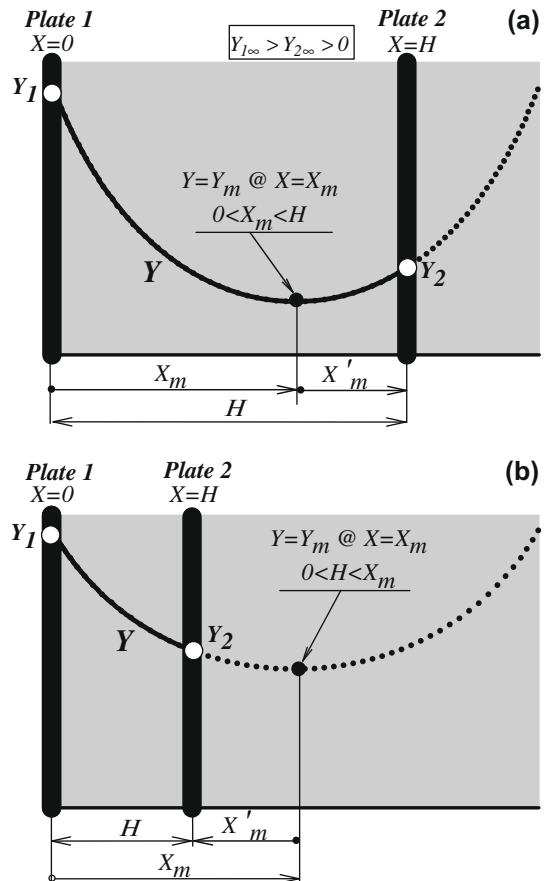


Fig. 2. Physical significance of parameters  $X_m$  and  $X'_m$ .

It should be emphasized that  $X_m$  and  $X'_m$  depend only on  $(S_1, Y_1)$  and  $(S_2, Y_2)$ , respectively, since  $\phi = S_1^2 - 2 \cosh Y_1 = S_2^2 - 2 \cosh Y_2$  from Eq. (9). Hence, Eq. (35) is extremely important since it explicitly relates the surface potentials and surface charge densities on both plates to the plate separation  $H$  in an easily calculable way without any need for linearization or cumbersome computational procedures. As explained above,  $Y_1$  and  $Y_2$  will always be constant and equal to  $Y_{1\infty}$  and  $Y_{2\infty}$  for all  $H$  for constant-potential surfaces. Expressing  $S_1$  in terms of  $S_2$  as  $S_1^2 = S_2^2 - 2 \cosh Y_{2\infty} + 2 \cosh Y_{1\infty}$  leaves only  $S_2$  and  $H$  as unknowns in Eq. (35). Then, for any physically meaningful value of  $S_2$ , the equation will yield a corresponding  $H$  value. The  $S_2$  values should be between the surface charge density at infinite separation and an arbitrary large negative surface charge density which would develop on Plate 2 at very close distances.

Similarly, for constant-charge surfaces, the  $S_{1\infty}$  and  $S_{2\infty}$  values will remain constant for all  $H$ . Remember from Eq. (8) that the surface charge densities at infinite separation can be obtained from the surface potentials at that separation. Also,  $Y_1$  can be expressed in terms of  $Y_2$  such that  $Y_1 = \cosh^{-1} \left( \frac{S_{1\infty}^2 - S_{2\infty}^2 + 2 \cosh Y_2}{2} \right)$ . This leaves only  $Y_2$  and  $H$  as unknowns in Eq. (35). Again, for any meaningful  $Y_2$  value entered, a corresponding  $H$  value will result. In this case, the  $Y_2$  values should be selected between the surface potential at infinite separation ( $Y_{2\infty}$ ) and an arbitrary large positive surface potential which would develop at very close distances.

Evaluating Eq. (4) at  $X_m$  shows that  $\phi = -2 \cosh Y_m$ . Also, from Eq. (9), it can be seen that  $Y_m = \cosh^{-1}(\cosh Y_1 - 0.5S_1^2)$ . Remembering that  $\phi = \sqrt{2} \cosh Y + \phi$  and inserting  $\phi = -2 \cosh Y_m$  in

Eq. (30) will show immediately that  $\Phi = X_m$  and will result in the expression

$$X_{1,2} = X_m \pm \lambda(\phi, \phi) \tag{36}$$

or more clearly

$$\begin{aligned} X_1 &= \lambda(S_1, \phi) - \lambda(\phi, \phi) \\ X_2 &= \lambda(S_1, \phi) + \lambda(\phi, \phi) \end{aligned} \tag{37}$$

Eq. (36) relates potential  $Y$  to location  $X$  in the EDL in an easily calculable way. The physical reason for the presence of the plus-minus double calculation in the above equation is the fact that the same potential  $Y$  will develop on the left and right arms of the potentials profile (on locations  $X_1$  and  $X_2$ ) on either sides of  $X_m$ .

In the following section, illustrative examples will be presented for surface potential, surface charge density, and electrostatic pressure calculations as a function of  $H$  for constant-potential and constant-charge scenarios for arbitrarily charged systems. The results of the calculations of the EDL potential profile  $Y$  as a function of  $X$  will also be presented and will be compared with numerical solutions of the PBE.

#### 4. Evaluation of the analytical expressions for different charging scenarios

Before presenting the example calculations and comparison of the above analytical equations with numerical computations, a table is presented in Appendix A to illustrate the ease of their use in calculating  $H$  and  $F_e$  for a selected charging condition as well as  $X$  vs. potential  $Y$  within the EDL.

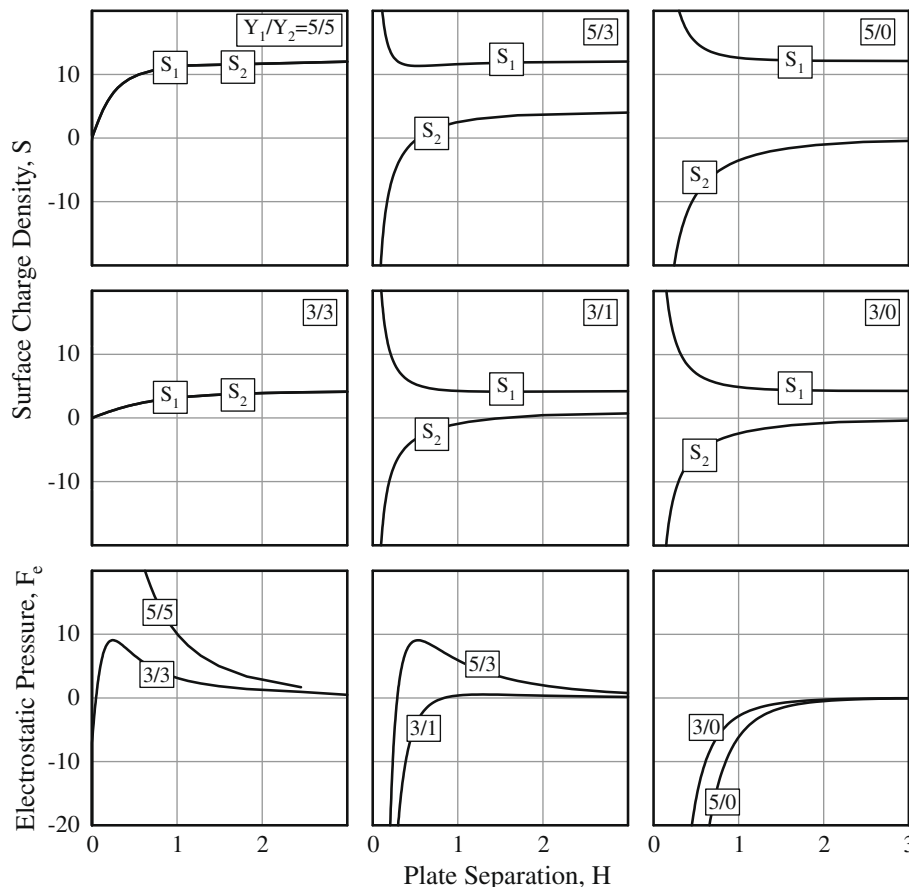


Fig. 3. Surface charge densities and electrostatic pressures as a function of plate separation for constant-potential surfaces for various surface potentials at infinite separation ( $Y_{1\infty}/Y_{2\infty} = 5/5, 5/3, 5/0, 3/3, 3/1,$  and  $3/0$  (calculated analytically using Eqs. (21) and (35)).

Fig. 3 gives the surface charge densities (the top two row graphs) from Eq. (35) and electrostatic pressures (the bottom row graphs) from Eq. (21) as a function of plate separation for constant-potential surfaces for various surface potentials at infinite separation ( $Y_{1\infty}/Y_{2\infty} = 5/5, 5/3, 5/0, 3/3, 3/1, \text{ and } 3/0$ ). The surface potentials at infinite separation which remain constant during the approach of the plates are given in each graph. The surface charge densities on both plates ( $S_1$  and  $S_2$ ), on the other hand, change with the separation between the plates. It can be seen that the charges on both plates vary identically for symmetrically charged plates ( $Y_{1\infty}/Y_{2\infty} = 5/5$  and  $3/3$  cases). However, for asymmetrical plates ( $Y_{1\infty}/Y_{2\infty} = 5/3$  and  $5/0, 3/1, \text{ and } 3/0$  cases), even though both plates start off with positive surface charges, the charge on the second plate reverses at close approach. The effect of this reversal can be seen in the bottom figures where electrostatic pressures are plotted as a function of plate separation. The electrostatic force is almost always repulsive for symmetrically charged plates. But, it becomes strongly attractive for asymmetrically charged plates due to the charge reversal taking place at close separations.

Fig. 4 presents the surface potentials (top two row graphs from Eq. (35) and electrostatic pressures (the bottom row graphs from Eq. (21) as a function of plate separation for constant-charge surfaces for the same surface potentials at infinite separation in Fig. 3. Under these surface conditions, the surface charge densities at infinite separation remain constant during the approach (given in the boxes in each graph) while the surface potentials change. It can be seen that potentials asymptotically approach

the  $Y_{1\infty}/Y_{2\infty}$  values at large separations. However, they become very large as separation between the plates decreases. Since the surface charge densities on both plates remain positive for all separations, the electrostatic force of interaction is repulsive for all initial conditions and for all separations.

Fig. 5 gives the potential profile  $Y$  as a function of  $X$  for plate separations of  $H = 4$  and  $H = 1$  for the same surface conditions used in Figs. 3 and 4 ( $Y_{1\infty}/Y_{2\infty} = 5/5, 5/3, 5/0, 3/3, 3/1, \text{ and } 3/0$  cases). The lines in these graphs are obtained by Eq. (36). The same conditions were also used in the numerical analysis by a shooting method and the results are presented as filled circles in the same graphs (see Appendix B for the core Mathematica code for this procedure). The figure demonstrates the validity of the analytical expressions developed in this paper for plates of arbitrary potentials with the sole constraint that plate potentials at infinite separation have the same sign.

Once the potential profile is known between the two plates, one can calculate the osmotic and Maxwell pressure components using Eq. (20b). This has been done for the  $Y_1/Y_2 = 5/3$  case for the plate separation of  $H = 1$  using the potential values obtained from Eq. (36) (see Fig. 5) and the results are presented in Fig. 6. It can be seen that the Maxwell pressure becomes almost negligible away from the plates where the electrostatic effect is least felt and the pressure at this point is mainly due to the osmotic component. Fig. 6 also shows that the overall pressure between the plates is always constant at all  $X$  which is why calculating the pressure on any one of the plates is sufficient as stated by Eq. (21).

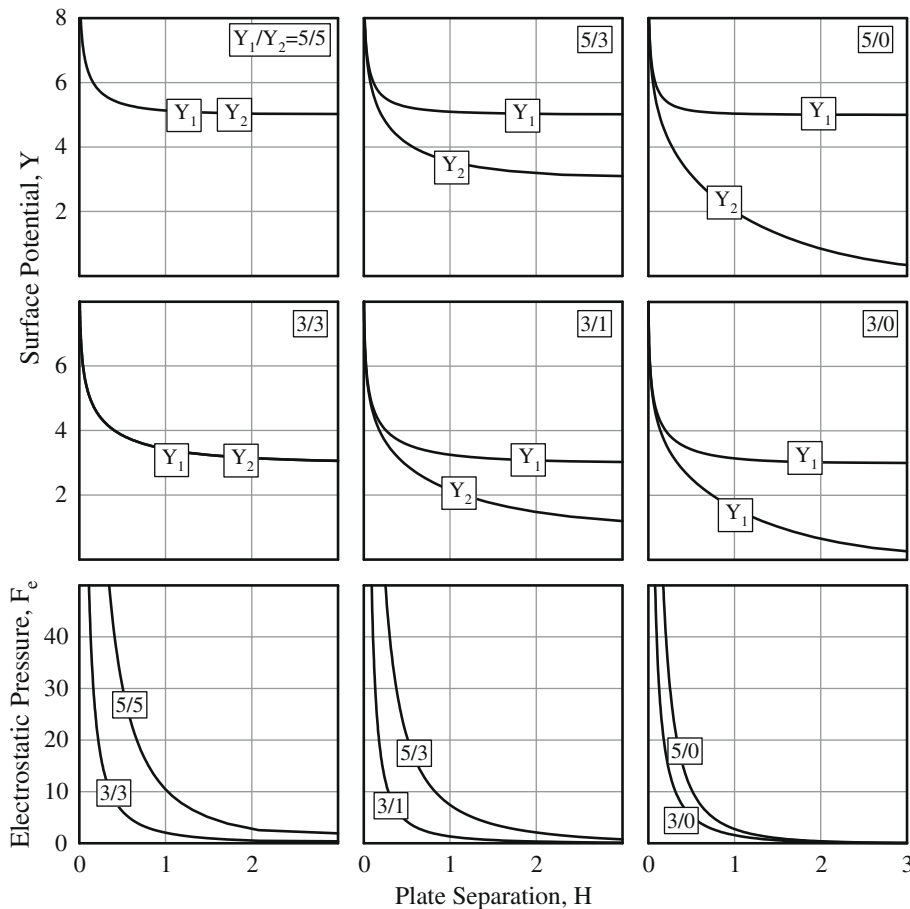


Fig. 4. Surface potentials and electrostatic pressures as a function of plate separation for constant-charge surfaces for various surface potentials at infinite separation ( $Y_{1\infty}/Y_{2\infty} = 5/5, 5/3, 5/0, 3/3, 3/1, \text{ and } 3/0$ ) (calculated analytically using Eqs. (21) and (35)).

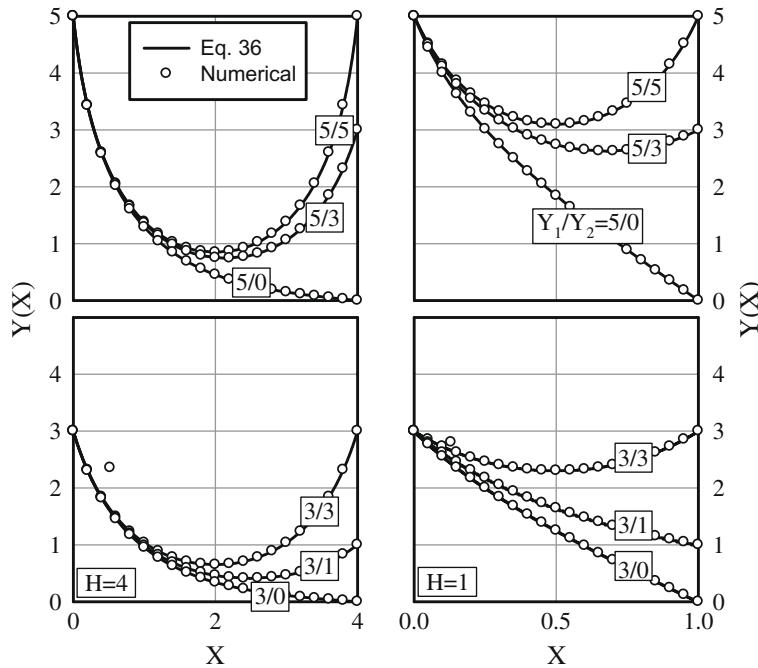


Fig. 5. Potential profiles for  $H = 4$  and  $H = 1$  for surface potentials of  $Y_1/Y_2 = 5/5, 5/3, 5/0, 3/3, 3/1,$  and  $3/0$ . The lines are calculated from Eq. (36) whereas the open circles are computed numerically using the shooting procedure for 20 points for each data set.

5. Summary

A compact analytical solution of the one-dimensional nonlinear Poisson–Boltzmann equation is presented for asymmetrically charged plates of arbitrary potentials interacting in symmetrical electrolyte solutions with the constraints that the plate potentials at infinite separation have the same sign.

The analytical expressions developed allow the calculation of

- surface potentials, surface charge densities, and electrostatic pressures as a function of plate separation (Eq. (35)) and
- potential profile in the EDL for a given plate separation (Eq. (36))
- osmotic and Maxwell pressures in the EDL (Eq. (20))

for different charging scenarios without any need for cumbersome numerical computations. Comparison of the potential pro-

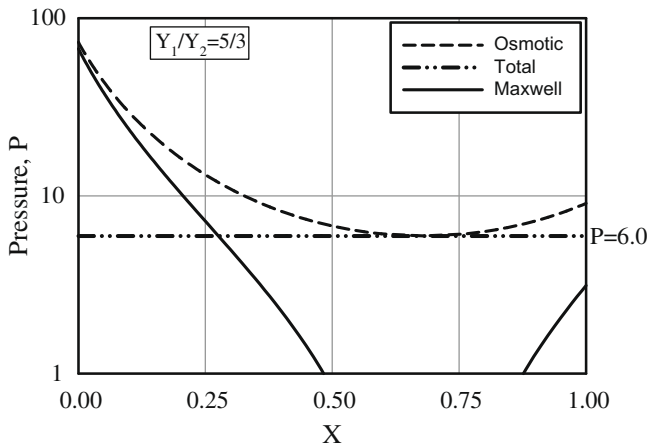


Fig. 6. Variation of osmotic and Maxwell pressure components within electrical double layer and the constancy of the overall pressure between the two plates. The lines were calculated using Eq. (20) from the analytical potential profile  $Y_1/Y_2 = 5/3$  and  $H = 1$  (see Fig. 5).

files obtained from the analytical expressions with those computed by numerical analysis demonstrates clearly the ease of use and the validity of the solution method developed in this paper.

Appendix A

Illustration of the use of analytical equations for an example double layer system assuming constant surface potentials of  $Y_1 = 5$  and  $Y_2 = 3$  (constant-potential surfaces).

(a) Calculation of interplate distance  $H$  and electrostatic pressure  $F_e$  at that  $H$

(i) Enter an arbitrary surface charge density for Plate 2:

$$S_2 = 4$$

(ii) Calculate from  $\phi = S_2^2 - 2 \cosh Y_{2\infty}$  and  $S_1$  from

$$S_1^2 = \cosh Y_{1\infty} + \phi \text{ for } S_2 = 4:$$

$$\phi = -4.135; S_1 = 12.012$$

(iii) Calculate  $H$  from  $H = X_m + X'_m$ :

$$X_m = \lambda(S_1, \phi) = \int_0^1 \frac{S_1}{\sqrt{u(S_1^2 u - \phi)^2 - 4u}} du$$

$$X'_m = \lambda(S_2, \phi) = \int_0^1 \frac{S_2}{\sqrt{u(S_2^2 u - \phi)^2 - 4u}} du$$

$$X_m = 1.458; X'_m = 1.160; H = 2.618$$

(iv) Calculate  $F_e$  on Plate 2 at  $H = 2.618$ :

$$F_e = \cosh Y_{2\infty} - 1 - \frac{S_2^2}{2}$$

$$F_e = 1.068$$

(v) Repeat steps (i)–(iv) for a range of  $S_2$  values to obtain  $S_1$ ,  $S_2$ , and  $F_e$  as a function of  $H$ .

**(b) Calculation of X vs. Y within the EDL at the calculated  $H = 2.618$**

(i) Enter an arbitrary potential  $Y$  between 0 and  $Y_{1\infty}$  within the EDL

$$Y = 2$$

(ii) Calculate  $\phi$  from  $\phi = \sqrt{2 \cosh Y + \phi}$  for  $Y = 2$  and  $\phi = -4.135$

$$\phi = 1.841$$

(iii) Calculate the locations  $X_1$  and  $X_2$  where potential  $Y = 2$  develops for  $X_m = 1.458$

$$X_{1,2} = \lambda(S_1, \phi) \pm \lambda(\phi, \phi) = X_m \pm \int_0^1 \frac{\phi}{\sqrt{u(\phi^2 u - \phi)^2 - 4u}} du$$

$$\lambda(\phi, \phi) = 0.795$$

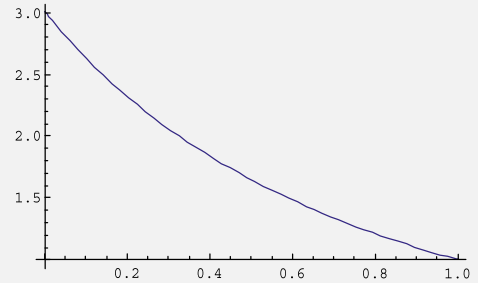
$$X_1 = 0.663; X_2 = 2.253$$

(iv) Repeat (i)–(iii) for a range of  $Y$  values to obtain graphs of  $Y$  vs.  $X$  for different  $H$

Line 5 `FindRoot[fpS[S] 1.0, {S, {S1, Su}}]`  
`{S → {-4.2229, -4.2229}}`  
 For  $Y_2 = 1.0$  determines the actual slope from the range in Line 5 by interpolation. The output which is -4.229 for this case is the charge density  $S$  for  $Y_1 = 3$  and  $Y_2 = 1.0$

Line 6 `NDSolve[{f'' [Y] Sinh[f[Y]], f[0] 3.0,`  
`f' [0] -4.2229}, f, {Y, 0, H}]`  
 This is the actual numerical solution line for potential value of  $Y_1 = 3$  and the surface charge  $S_1 = 4.229$  determined by the shooting in order to obtain the potentials profile.

Line 7 `Plot[Evaluate[f[Y]/.%], {Y, 0, H}, PlotRange → All]`



Plots the potential profile as a function of  $X$  for given  $H$ .  $Y_1$ ,  $Y_2$ ,  $S_1$  and  $S_2$  values determined from this plot can be employed to calculate electrostatic pressure at that  $H$ .

## Appendix B

The core Mathematica algorithm for numerical evaluation of the one-dimensional nonlinear Poisson–Boltzmann equation to calculate the potential profile between two plates.

Line 1 `H=1;S1=-3.;Su=-7;Si=(Su-S1)/50//N;`  
 Defines separation as  $H=1$  and the “shooting” range for  $dY/dX$  on Plate 1 between  $S_1=-3$  and  $S_u=-7$  using increment  $Si$ . The initial values of the  $S_1$  and  $S_u$  must be estimated with care since the “shooting” procedure goes out of bounds of conditions on Plate 2.

Line 2 `fpend[S_]:=f[H]/.NDSolve[{f'' [Y] sinh[f[Y]],`  
`f[0] 3.0,f' [0] S},f,{Y,0,H}]`  
 Starts “shooting” by numerically solving the differential equation  $\frac{d^2 Y}{dX^2} = \sinh Y$  for  $S$  values between  $S_1$  and  $S_u$  for a surface potential of  $Y=3.0$  on the first plate. It stores the  $Y$  value obtained on the second plate for each  $S$

Line 3 `Table[{S,fpend[S]},{S,S1,Su,Si}]`  
 Pairs the  $S$  estimates and the corresponding solutions together in a range

Line 4 `fpS=Interpolation[%];fpS[S]`  
 Obtains and interpolation of the above range and assigns it to a function

Line 5 `lst2={-20,-20,-14,-10,-8,-5.7,-4,-2.8,-2,-1.4,-1,`  
`-.8,-.57,-.4,-.28,-.2,-.14,-.1,-.08,-.057,-.04,-.028,`  
`-.02,-.014,-.01,0,.01,.014,.02,.028,.04,.057,.08,.1,`  
`.14,.2,.28,.4,.57,.8,1,1.4,2,2.8,4,5.7,8,10,14,20,20}`  
 Interpolation range for  $Y$

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