A Simple Algorithm for Calculating Electrical Double Layer Interactions in Asymmetric Electrolytes—Poisson–Boltzmann Theory

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A simple, general, and numerically robust algorithm is presented for calculating the disjoining pressure and interaction free energy per unit area between two identically charged flat plates due to electrical double layer interactions according to the nonlinear Poisson–Boltzmann theory. The result is applicable to electrolytes with any number of ionic species having any combination of valencies as well as to constant potential, constant charge, or charge regulation boundary conditions on the plates. The algorithm is very simple to implement on commonly available numerical software environments and is therefore particularly suitable for use in data analysis. © **2002 Elsevier Science**

The nonlinear Poisson–Boltzmann theory provides an accurate mean field description of electrical double layer interactions in the colloidal regime and it is used extensively in interpreting direct and indirect measurements of colloidal forces. For interactions involving symmetric electrolytes the problem has been studied extensively (1). For mixed valence systems, only specific cases have been analyzed and the solutions are not simple to implement. It is therefore most desirable to have a simple, general and robust method of calculating electrical double layer interactions for all electrolyte compositions.

Consider two identical, uniformly charged planar surfaces located at $x = -L/2$ and at $x = L/2$ (a distance L apart) separated by an electrolyte solution in contact with a bulk reservoir that comprises n_i ions per unit volume of species i with valence v_i. The mean electrostatic potential $\psi(x)$ obeys the nondimensional Poisson–Boltzmann equation

$$\frac{d^2 y}{d\xi^2} = -\sum_i \alpha_i v_i \exp(-v_i y), \quad -\kappa L/2 \leq \xi \leq \kappa L/2, \quad [1]$$

with $y(\xi) = e\psi(x)/kT$, the potential scaled by the protonic charge e and the thermal energy kT; and $\xi = \kappa x$, the coordinate scaled by the Debye parameter $\kappa \equiv (n_o e^2/\varepsilon_0 \varepsilon_r kT)^{1/2}$ of the electrolyte with ionic strength $n_o \equiv \sum_j n_j v_j^2$ and ion number ratios $\alpha_i \equiv n_i/n_o$. The scaled surface potential of each plate is $y(\kappa L/2) = z$. At the median plane $x = 0$, where $dy/dx = 0$

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because of symmetry, the potential is $y(0) = u$. Without loss of generality, we can assume $z \geq u \geq 0$ provided the concentrations and the signs of the valencies of all the asymmetric ionic species are adjusted accordingly.

Herewith the key results while details of the derivation are deferred to the latter part of this article. After application of the boundary condition at the median plane $\xi = 0$, the first integral of [1]

$$\frac{dy}{d\xi} = 2^{1/2} \left\{ \sum_i \alpha_i [\exp(-v_i y) - \exp(-v_i u)] \right\}^{1/2} \quad [2]$$

can be integrated from $\xi = 0$ to $\kappa L/2$, that is, from $y = u$ to z, to give

$$\kappa L = 2^{1/2} \int_u^z \frac{dy}{\left\{ \sum_i \alpha_i [\exp(-v_i y) - \exp(-v_i u)] \right\}^{1/2}} \quad [3a]$$

$$\equiv \int_0^{\sqrt{z-u}} \frac{2s \, ds}{G(s^2 + u, u)}, \quad [3b]$$

where

$$G(x, y)$$
$$\equiv \left\{ -\sum_i \alpha_i \exp\left[-\frac{1}{2} v_i(x+y) \right] \sinh\left[\frac{1}{2} v_i(x-y) \right] \right\}^{1/2}. \quad [4]$$

The disjoining pressure $P(L)$ is given, as usual, in terms of the median plane potential u:

$$P(L) = kT \sum_i n_i \{\exp[-v_i u] - 1\} \equiv 2n_o kT [G(u, 0)]^2. \quad [5]$$

The interaction free energy per unit area can be obtained by integrating the disjoining pressure $P(L)$ [5] with respect to the separation L.

307

The results given thus far are completely general and are independent of boundary conditions on the surfaces. However, expressions for the interaction free energy per unit area will vary with the type of boundary conditions:

(i) For surfaces that interact under *constant surface potential*, where the surface potential z is independent of the median plane potential u, the interaction free energy per unit area $V_P(L)$ is

$$V_P(L) = \frac{n_o kT}{\kappa}\left\{-2\kappa L[G(u,0)]^2 + 4\int_0^u G(y,0)\,dy \right.$$

$$\left. +4\int_u^z [G(y,0) - G(y,u)]\,dy \right\}. \qquad [6]$$

The following remarks are in order:

(a) Equations [3]–[6] express the separation, L, the disjoining pressure, $P(L)$, and the interaction free energy per unit area, $V_p(L)$, parametrically in terms of the median plane potential u. These are to be used to generate the triplet $\{L, P(L), V_P(L)\}$ for a suitable range of values u. An evenly spaced set of u values between 0 and z is sufficient for almost all practical applications.

(b) The integrands in Eqs. [3] and [6] are well behaved throughout the domains of integration; in particular, the integrand in Eq. [3b] is finite at the lower limit $s = 0$ so that no special numerical integration methods are required. Furthermore, the functions and the integrals have been arranged and grouped to minimize loss of significant figures at extreme values of the parameters, e.g., as $L \to \infty$; that is, $u \to 0$.

(c) By using list handling capabilities and adaptive numerical integration routines of software packages such as *Mathematica* (2), the entire algorithm can be implemented in a few lines of code, see Table 1 (3). If $P(L)$ and $V_P(L)$ are needed as functions of L, the data pairs $\{L, P(L)\}$ and $\{L, V_P(L)\}$ can be used to construct interpolation functions (4). The function $G(x, y)$ is used throughout to take advantage of the precision of built-in intrinsic forms of the hyperbolic sine function.

(ii) For surfaces that interact under *constant surface charge*, the surface potential z for a given value of the median plane potential u has to be found by first solving the equation

$$G(z, u) = G(z_\infty, 0), \qquad [7]$$

where the constant surface charge density is characterized in terms of the scaled surface potential at infinite separation, z_∞. Equation [7] has a unique root located in $\max(u, z_\infty) \le z < \infty$. Once z is found for a given value of u, Eqs. [3] and [5] will give the separation, L, and the disjoining pressure, $P(L)$, while the interaction free energy per unit area under constant charge

$V_C(L)$ is given by

$$V_C(L) = \frac{n_o kT}{\kappa}\left\{-2\kappa L[G(u,0)]^2 + 4\int_0^u G(y,0)\,dy \right.$$

$$+4\int_u^z [G(y,0) - G(y,u)]\,dy + 4(z - z_\infty)G(u_\infty, 0)$$

$$\left. -4\int_{z_\infty}^z G(y,0)\,dy \right\} \qquad [8]$$

(iii) For surfaces that interact under *charge regulation*, the scaled surface potential z has to be found using the surface charge–surface potential relationship $\sigma(z)$ that characterizes the charge regulation process. For a given median plane potential, u, the surface potential, z, has to be obtained by first solving the equation

$$2G(z, u) = \frac{e\sigma(z)}{\varepsilon_0 \varepsilon_r kT\kappa}, \qquad [9]$$

which has a unique solution for $z > 0$. Using this solution, Eqs. [3] and [5] will give the seperation L and the disjoining pressure $P(L)$, while the interaction free energy per unit area under charge regulation $V_R(L)$ is

$$V_R(L) = \frac{n_o kT}{\kappa}\left\{-2\kappa L[G(u,0)]^2 \right.$$

$$+4\int_0^u G(y,0)\,dy + 4\int_u^z [G(y,0) - G(y,u)]\,dy$$

$$\left. +2\frac{e}{\varepsilon_0 \varepsilon_r kT\kappa}\int_{z_\infty}^z \sigma(y)\,dy - 4\int_{z_\infty}^z G(y,0)\,dy \right\}. \qquad [10]$$

For large separations, $\kappa L \gg 1$, results for the different boundary conditions all approach those obtained from the so called *superposition approximation* or *weak overlap approximation*. Far from an isolated surface with surface potential z_∞, the potential has the asymptotic form $\psi(x) \cong (kT/e)A z_\infty e^{-\kappa x}$, $\kappa x \gg 1$. From this result, we obtain the disjoining pressure and the interaction energy valid for $\kappa L \gg 1$:

$$P(L) \cong n_o kT\left\{2z_\infty^2 A^2 e^{-\kappa L}\right\}$$

$$V(L) \cong \frac{n_o kT}{\kappa}\left\{2z_\infty^2 A^2 e^{-\kappa L}\right\},$$

TABLE 1
Poisson–Boltzmann Plates—Asymmetric Electrolyte

■ Define functions for pressure and energy

```
G[x_, y_] := √-αi.( -vi (x+y)/2 Sinh[vi (x - y) / 2]) ;

xLasym[z_, u_] := NIntegrate[ (2 s)/(G[s² + u, u]) , {s, 0, √(z - u)}];

Pasym[u_] := 2 (G[u, 0])² ;

VasymP[z_, u_, κL_] := -2 κL (G[u, 0])² +
    4 NIntegrate[G[y, 0], {y, 0, u}] + 4 NIntegrate[G[y, 0] - G[y, u], {y, u, z}];

VasymC[z∞_, z_, u_, κL_] :=
    VasymP[z, u, κL] - 4 ( NIntegrate[G[y, 0], {y, z∞, z}] - G[z∞, 0] (z - z∞));
```

■ Constant potential sample calculation

```
vi = {1, -1, 1, -2}; (* valence of ionic species *)
ci = {0, 0, 2 10⁻³, 10⁻³}; (* molar concentration of ionic species *)
Print["Electroneutrality check: ", ci.vi];
αi = ci/(ci.(vi)²) ;

(* MKS Units for Pressure, Energy,
 Potential and Debye kappa- Pmks, Vmks, ψmks & κ *)

Block[{ T = 25 + 273, e = 1.602192 * 10⁻¹⁹, k = 1.380622 * 10⁻²³,
    ε = (8.85 10⁻¹²) 78.3, avo = 6.022 10²³, no}, no = 1000 avo ci.(vi)²;

    κ = √((no e²)/(ε k T)) ; Pmks = no k T; Vmks = Punit / κ; ψmks = (k T)/e;];

z∞ = 4.0; (* surface potential at infinite separation *)
u = 3.5; (* pick a value *)
z = z∞;
κL = xLasym[z, u];
Pres = Pasym[u];
Vp = VasymP[z, u, κL] ;
Print["Constant potential: κL = ", κL,
    " Pres = ", Pres, " Vp = ", Vp, " ysurf = ", z];
Print["Physical units: L(m) = ", κL/κ, " P(N/m²) = ",
    Pres Pmks, " Vp(J/m²) = ", Vp Vmks, " ψ(V) = ", z ψmks];
```

■ Constant charge sample calculation

```
vi = {1, -1, 1, -2}; (* valence of ionic species *)
ci = {0, 0, 2 10⁻³, 10⁻³}; (* molar concentration of ionic species *)
Print["Electroneutrality check: ", ci.vi];
αi = ci/(ci.(vi)²) ;

(* MKS Units for Pressure, Energy,
 Potential and Debye kappa- Pmks, Vmks, ψmks & κ *)

Block[{ T = 25 + 273, e = 1.602192 * 10⁻¹⁹, k = 1.380622 * 10⁻²³,
    ε = (8.85 10⁻¹²) 78.3, avo = 6.022 10²³, no}, no = 1000 avo ci.(vi)²;

    κ = √((no e²)/(ε k T)) ; Pmks = no k T; Vmks = Punit / κ; ψmks = (k T)/e;];

z∞ = 4.0; (* surface potential at infinite separation *)
u = 3.5; (* pick a value *)
z = z /. FindRoot[G[z, u] == G[z∞, 0], {z, {Max[u, z∞], 6 z∞}}];
κL = xLasym[z, u];
Pres = Pasym[u];
Vc = VasymC[z∞, z, u, κL];
Print["Constant charge: κL = ", κL,
    " Pres = ", Pres, " Vc = ", Vc, " ysurf = ", z];
Print["Physical units: L(m) = ", κL/κ, " P(N/m²) = ",
    Pres Pmks, " Vc(J/m²) = ", Vc Vmks, " ψ(V) = ", z ψmks];
```

where the constant A is given by

$$\log A \equiv \int\limits_{0}^{z_\infty} \frac{y - 2G(y, 0)}{2yG(y, 0)}\, dy.$$

This completes the specification of the method for calculating electrical double layer interactions involving asymmetric electrolytes between identical plates for all common boundary conditions. With modern numerical computation software packages, this method of calculating the separation L, the disjoining pressure $P(L)$, and the interaction energy per unit area $V(L)$ is very easy to implement.

We now give details of the derivation of the above results. The function $G(x, y)$ which follows from the identity

$$e^{-x} - e^{-y} = -2e^{-(x+y)/2} \sinh[(x - y)/2] \qquad [11]$$

is used to obtain Eq. [3b] from [3a] in order to circumvent the potential loss of significant figures in [3a]. A similar transformation is used to ensure that the disjoining pressure in Eq. [5] is evaluated accurately for small u. In Eq. [3a], the change to the new integration variable s defined by $y = s^2 + u$ in Eq. [3b] removes the integrable inverse square root singularity at the lower limit $y = u$.

The derivation of the interaction free energy at constant potential $V_P(L)$ requires an integration by parts

$$V_P(L) = -\int\limits_{\infty}^{L} P(L)\, dL = -P(L)\, L + \int\limits_{0}^{u} L \frac{dP}{du}\, du, \qquad [12]$$

where dP/du is obtained from Eq. [5], while Eq. [3a] is used to replace L in the same integrand to obtain a double iterated integral. If the surface potential z is a constant, an interchange in the order of integration together with a regrouping of terms gives the final result in [6] after using [11].

At any value of u, the additional equation to be solved for the surface potential z for constant surface charge [7] or for charge regulation [9] surfaces follows from applying the usual electrostatic Gaussian boundary condition to Eq. [2] at $x = L/2$, the surface of the plate.

The derivation of the interaction free energies $V_C(L)$ [8] and $V_R(L)$ [10] from $V_P(L)$ [6] is a straightforward generalization of a similar derivation for 1:1 electrolytes (5).

In the case of 1:1 or symmetric electrolytes, it is more efficient to use the following explicit forms of Eqs. [3]–[6] (1, 5)

$$\kappa L = 4m[K(m) - F(\varphi \,|\, m)], \qquad [11]$$

where $m = e^{-2u}$ and $\varphi = \arcsin(e^{-(z-u)/2})$; and $K(m)$ and $F(\varphi \,|\, m)$ are elliptic integrals of the first kind and are readily available (6). The disjoining pressure $P(L)$ in [5] becomes

$$P(L) = 2n_okT \sinh^2 \frac{1}{2} u, \qquad [12]$$

and the expression for the interaction free energy per unit area

[6] for *constant potential* surfaces becomes

$$V_P(L) = \frac{n_okT}{\kappa} \left\{ 16 \sinh^2 \frac{1}{4} u - \kappa L \left[\sinh u + 2e^{u/2} \sinh \frac{1}{2} u \right] \right.$$
$$- 8 \left[\sinh \frac{1}{2}(z - u) \sinh \frac{1}{2}(z + u) \right]^{1/2}$$
$$\left. - 8e^{u/2} \left[E(\varphi, m) - E\left(\frac{\pi}{2}, m\right) \right] \right\}, \qquad [13]$$

where $E(\varphi, m)$ is the elliptic integral of the second kind (6). For *constant charge* surfaces the expression for the interaction free energy per unit area, $V_C(L)$ [8], is given by

$$V_C(L) = \frac{n_okT}{\kappa} \left\{ 16 \sinh^2 \frac{1}{4} u - \kappa L \left[\sinh u + 2e^{u/2} \sinh \frac{1}{2} u \right] \right.$$
$$- 8 \left[\sinh \frac{1}{2}(z - u) \sinh \frac{1}{2}(z + u) \right]^{1/2}$$
$$- 8e^{u/2} \left[E(\varphi, m) - E\left(\frac{\pi}{2}, m\right) \right]$$
$$+ 4(z - z_\infty) \sinh \frac{1}{2} z_\infty$$
$$\left. - 16 \sinh \frac{1}{4}(z - z_\infty) \sinh \frac{1}{4}(z + z_\infty) \right\}, \qquad [14]$$

and the explicit solution of [7] for the surface potential z is

$$z = \operatorname{arcosh}\left(2 \sinh^2 \frac{1}{2} z_\infty + \cosh u\right). \qquad [15]$$

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2. *Mathematica* is a trademark of and is available from Wolfram Research, Inc., 100 Trade Center Drive, Champaign, IL 61820-7237.
3. An electronic version of the *Mathematica* code is available from the author.
4. Lists of the data pairs $\{\kappa L, P(L)\}$ and $\{\kappa L, V(L)\}$ can be generated parametrically in u and the results can be used to create callable functions for $P(L)$ and $V(L)$ using the built-in `Interpolation[`*list*`]` function in *Mathematica*.
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