

A Simple Algorithm for the Calculation of the Electrostatic Repulsion between Identical Charged Surfaces in Electrolyte

I. INTRODUCTION

The colloid scientist is often required to calculate the electrical double-layer interaction between charged surfaces in order to compare theory and experiment. For example, recent experimental measurements of forces between charged surfaces in electrolyte (1) are of sufficiently high precision to require the most precise calculation of the electrostatic repulsion in a variety of electrolyte solutions and boundary conditions (e.g., constant surface charge or constant surface potential).

The traditional calculation of the double-layer interaction is involved. It requires the analytic solution of the nonlinear Poisson-Boltzmann equation between parallel half spaces in terms of elliptic functions and the subsequent numerical solution of a complex transcendental equation. Not surprisingly, this has led to the extensive use of tables (2, 3) which are available for only selected values of the surface charge or potential and electrolyte concentrations and valences. This restriction means that in most practical cases, one must interpolate from the tables. In spite of the complexities and inconveniences, the tables remain in common use.

This note attempts to present a fast numerical procedure which is capable of computing the electrostatic interaction across symmetric electrolytes with high precision for any of the commonly encountered boundary conditions.

II. THE METHOD

For simplicity, we will discuss the numerical procedure for a 1:1 electrolyte between identical, charged, plane-parallel interfaces. The planar Poisson-Boltzmann equation for the scaled potential Y ($e\psi/kT$) in a 1:1 electrolyte solution of number concentration n is

$$\frac{d^2 Y}{dX^2} = \sinh Y, \quad [2.1]$$

where X (κx) is the scaled distance measured from the midplane (Fig. 1) and

$$\kappa^2 = \frac{8\pi n e^2}{\epsilon kT}. \quad [2.2]$$

A first integration yields

$$\frac{dY}{dX} = Q \operatorname{Sgn}(Y_m), \quad [2.3]$$

where we define the variable Q by

$$Q = (2(\cosh Y - \cosh Y_m))^{1/2}, \quad [2.4]$$

where Y_m is the scaled midplane potential. Equation [2.3] satisfies the zero-derivative boundary condition at $X = 0$ (Fig. 1). We note that

$$\begin{aligned} \frac{dQ}{dY} &= \frac{\sinh Y}{Q} \\ &= \frac{\operatorname{Sgn}(Y_m) \left[\left(\frac{Q^2}{2} + \cosh Y_m \right)^2 - 1 \right]^{1/2}}{Q}. \end{aligned} \quad [2.5]$$

From Eqs. [2.3] and [2.5] we derive the differential equation

$$\frac{dX}{dQ} = \left[\left(\frac{Q^2}{2} + \cosh Y_m \right)^2 - 1 \right]^{-1/2}. \quad [2.6]$$

The midplane in terms of these variables is the point ($Q = 0, X = 0$). If we know what value of Q ($=Q_s$) corresponded to the surface of charge, then for a given value of the reduced midplane potential Y_m , we can solve Eq. [2.6] from $Q = 0$ to $Q = Q_s$ by a suitable numerical technique (e.g., a fourth-order Runge-Kutta method (4)). Thus we determine $X_s = \kappa L/2$, the scaled distance from the midplane to the surface of charge corresponding to the given value of Y_m . Repeating this procedure for a set of suitably chosen values of Y_m (see below) will generate a set of corresponding $\kappa L/2$ values. The electrostatic pressure at each value of L is simply calculated from the corresponding Y_m value by

$$P(L) = 2nkT(\cosh Y_m - 1). \quad [2.7]$$

The interaction free energy per unit surface area $E_p(L)$ can be computed from

$$E_p(L) = \int_L^\infty P(L') dL' \quad [2.8]$$

using a numerical quadrature formula (see below). The interaction free energy for spherical surfaces $E_{sp}(L)$ with radii a_1 and a_2 at separation L can be computed by a similar numerical quadrature directly from the pressure, Eq. [2.7], if the Derjaguin approximation is invoked:

$$\begin{aligned} E_{sp}(L) &\approx \frac{2\pi a_1 a_2}{a_1 + a_2} \int_L^\infty dL' E_p(L') \\ &= \frac{2\pi a_1 a_2}{a_1 + a_2} \int_L^\infty dL' (L' - L) P(L'). \end{aligned} \quad [2.9]$$

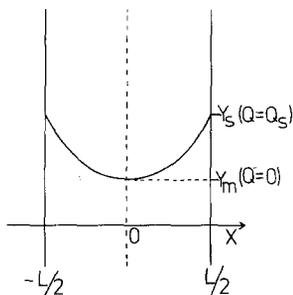


FIG. 1. The potential profile between identical planar double layers.

This result should be a good approximation for κa_1 , $\kappa a_2 \geq 10$. There are some finer points to the calculation of these integrals and the choice of Y_m values to which we return in Section III.

It remains to indicate how the surface Q value, viz., Q_s , is determined. This is dependent on the type of boundary conditions invoked.

(i) Constant Surface Potential Y_s

In this case, Q_s is calculated directly from definition [2.4] with $Y = Y_s$,

$$Q_s = [2(\cosh Y_s - \cosh Y_m)]^{1/2}. \quad [2.10]$$

(ii) Constant Surface Charge σ

At the right-hand surface we have the boundary condition

$$\frac{dY}{dX} = \frac{4\pi e}{\epsilon kT} \cdot \sigma. \quad [2.11]$$

From Eq. [2.3], we see immediately that

$$Q_s = \frac{4\pi e}{\epsilon kT} |\sigma|. \quad [2.12]$$

(iii) Surface Charge Regulation

When the surface charge is determined by the adsorption of a potential-determining ion onto specific surface sites, neither charge nor potential remains constant during interaction (5-7). Both Eqs. [2.10] and [2.12] still hold but σ and Y_s are not determined. To determine Q_s an extra equation is therefore necessary. Applying the mass-action principle to the surface adsorption process leads to another relationship between surface charge and surface potential. For example, for a surface weak-acid dissociation, we have (5)

$$\frac{|\sigma| 10^{-pH}}{eN_s - |\sigma|} = K_a e^{-Y_s}, \quad [2.13]$$

where N_s is the surface density of acid groups and K_a is the dissociation constant. Equations [2.10], [2.12], and [2.13] are sufficient to determine Q_s (and σ and Y_s) for a given Y_m .

III. OPTIMIZATION OF NUMERICAL QUADRATURE ACCURACY

In a constant potential interaction the scaled mid-plane potential varies smoothly from zero at $X = \infty$ to Y_s at $X = 0$. Clearly, one must choose the Y_m values from between these limits¹; the smallest Y_m value corresponding to the largest distance, L_{\max} , say. The numerical quadrature required to obtain the interaction free energy can be performed only over the range L to L_{\max} . By ensuring that the smallest Y_m value is such that $\kappa L_{\max} \geq 3$, we can perform the tail of the integration from L_{\max} to infinity analytically since the pressure $P(L)$ can be assumed to decay exponentially for $L \geq L_{\max}$.

If we decide on a total of N points (L, Y_m) between $(\infty, 0)$ and $(0, Y_s)$, then the simplest choice of the Y_m , viz., equally spaced values of Y_m , will produce unequally spaced ($L, P(L)$) values. With this choice of Y_m values, only a very unsophisticated quadrature formula (e.g., trapezoidal rule) can be used to evaluate the integrals in Eq. [2.8] or [2.9]; and, for accuracy, we would need to choose a very large value of N (≥ 100). This can be avoided by choosing the value of Y_m so that the pressure values are equally spaced between zero and P_{\max} (given by Eq. [2.7] with $Y_m = Y_s$). After an integration by parts, we can rewrite Eqs. [2.8] and [2.9] as

$$E_p(L) = \int_0^{P(L)} (L'(P') - L) dP' \quad [3.1]$$

and

$$E_{sp}(L) = \frac{\pi a_1 a_2}{a_1 + a_2} \int_0^{P(L)} (L'(P') - L)^2 dP'. \quad [3.2]$$

Because the points have been chosen so that the P values are equally spaced, we can use a much more accurate quadrature rule (e.g., an Adams extrapolation formula (4)). This enables us to use much fewer points to achieve comparable accuracy.

The method outlined above is easily generalized to the case of a general electrolyte solution containing mixtures of ions of different valence. Stern layer models can also be incorporated with some straightforward modification of the surface boundary condition

¹ For constant charge and regulated interactions the magnitude of the midplane potential Y_m can increase indefinitely. However, by the time Y_m has increased to $Y_s(\infty)$ (the value of the surface potential at infinite separation) we have $\kappa L \ll 1$. Thus $Y_s(\infty)$ provides a suitable scale on which to choose Y_m values for these types of interaction.

which determines Q_s . As a computational algorithm, the method possesses the advantages of speed, accuracy, and simplicity. A Fortran subroutine is available from the authors.

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