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# NOTE

## Interaction Free Energy between Plates with Charge Regulation: A Linearized Model

**The linearized Poisson–Boltzmann theory is used to calculate the electrical double layer interaction free energy between two parallel charged plates for the case in which charge regulation due to the dissociation of surface groups may be modelled by the linearized regulation model that specifies a linear relationship between the surface charge and the surface potential. This charge regulation model is characterized by a constant—termed the regulation capacitance of the surface. Analytic expressions for the force per unit area, the interaction free energy per unit area as well as the interaction free energy between two nonidentical spheres in the Deryaguin limit are given for the general case of nonidentical surfaces. An expression for the interaction free energy, applicable to any geometry, is obtained by thermodynamic arguments. Numerical comparisons for the case of identical amphoteric surfaces show that linearizing the charge regulation boundary conditions produces little error in the resultant interaction free energy.** © 1993 Academic Press, Inc.

## INTRODUCTION

We derive analytic expressions to describe the electrical double layer interaction between dissimilarly charged flat plates and spheres (in the Deryaguin limit) which have low to modest surface potentials based on the linearized Poisson–Boltzmann (Debye–Hückel) equation. As the separation between the surface changes, the interacting plates or spheres may in general be dissimilar and can maintain constant surface potential, constant surface charge or maintain chemical equilibrium of ionizable surface groups. We refer to the last case as charge regulating surfaces.

In all models for regulating surfaces, the surface charge–surface potential relation is nonlinear. Consistent with the linearized Poisson–Boltzmann equation, we propose a way to linearize this charge–potential relation which is accurate and also permits analytic solutions of various quantities of interest. We derive, for dissimilarly charged plates, expressions for the force per unit area and the interaction free energy per unit area, and we also apply the Deryaguin method to obtain the interaction between large particles. The constant charge and constant potential models emerge as special limits. The accuracy of this approach is examined by comparison with numerical solutions based on the linearized Poisson–Boltzmann equation and the nonlinear surface charge–surface potential relation that governs charge regulation.

## LINEARIZED REGULATION MODEL

We use an amphoteric surface as a concrete example; however, the final results can be applied to any model of charge regulation. Ionization of surface groups on an amphoteric surface is governed by the dissociation reactions

$$AH_2^+ \Leftrightarrow AH + H^+ \quad (K_+) \qquad [1]$$

$$AH \Leftrightarrow A^- + H^+ \quad (K_-) \qquad [2]$$

with specified dissociation constants $K_+$ and $K_-$. With $N_s$ such groups per unit area, the surface charge density $\sigma(\psi_s)$ can be written in terms of the surface potential $\psi_s$ as (1)

$$\sigma(\psi_s) = eN_s \frac{[AH_2^+] - [A^-]}{[AH] + [AH_2^+] + [A^-]} = eN_s \frac{\delta \sinh[e(\psi_N - \psi_s)/kT]}{1 + \delta \cosh[e(\psi_N - \psi_s)/kT]}, \qquad [3]$$

where

$$\delta = 2(K_-/K_+)^{1/2} \qquad [4a]$$

$$\psi_N = 2.303(kT/e)[\tfrac{1}{2}(pK_+ + pK_-) - pH]. \qquad [4b]$$

For an isolated surface, the surface potential $\psi_s^{iso}$ is determined by applying the boundary condition on the discontinuity of the displacement field

$$\left[\epsilon \frac{\partial\psi}{\partial n}\right] = -4\pi\sigma(\psi_s^{iso}), \qquad [5]$$

where the surface normal n is along the direction of the outward normal and $\epsilon$ is the dielectric constant. The normal derivative $(\partial\psi/\partial n)$ can be related to the surface potential $\psi_s^{iso}$ by integrating the Poisson–Boltzmann equation.

For a 1:1 electrolyte (with Debye screening parameter $\kappa$) against a plane charged surface, the Poisson–Boltzmann equation can be integrated to give

$$\frac{\partial\psi}{\partial n} = -\frac{2kT\kappa}{e}\sinh(e\psi_s^{iso}/2kT). \qquad [6]$$

Thus $\psi_s^{iso}$ is found by combining [5] and [6] and then solving the resulting equation

$$\sinh(e\psi_s^{iso}/2kT) = \frac{2\pi N_s e^2}{\kappa\epsilon kT}\frac{\delta \sinh[e(\psi_N - \psi_s^{iso})/kT]}{1 + \delta \cosh[e(\psi_N - \psi_s^{iso})/kT]}. \qquad [7]$$

The solution of this equation is the point of intersection between the two curves shown in Fig. 1.

The first ingredient of the linearized regulation model is the linear Debye–Hückel equation

$$\nabla^2\psi - \kappa^2\psi = 0 \qquad [8]$$

used to describe the electrostatic potential in the electrolyte. The expression for $\partial\psi/\partial n$ for an *isolated* surface will vary depending on the geometry of the surface. For a planar surface, we have

$$\frac{\partial\psi}{\partial n} = -\kappa\psi_s^{iso}, \qquad [9a]$$

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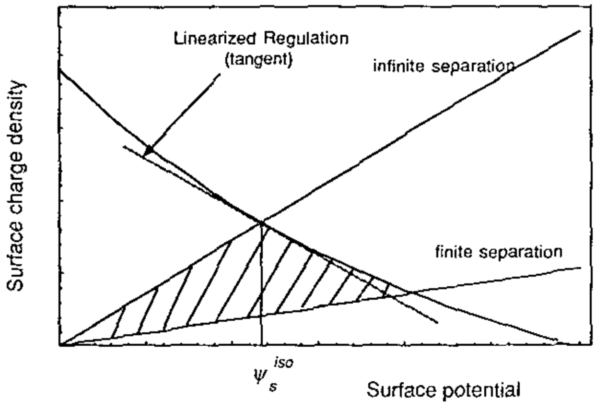

FIG. 1. Schematic representation of Eq. [7] for locating the surface potential of a surface in isolation $\psi_s^{\text{iso}}$. The shaded area is the interaction free energy (see Eq. [24]).

while for a sphere of radius $a$, we have

$$\frac{\partial\psi}{\partial n} = -\frac{1+\kappa a}{a}\psi_s^{\text{iso}} \qquad [9b]$$

where $\psi_s^{\text{iso}}$ is the constant surface potential of the isolated surface. This constant can be found by combining Eqs. [3], [5], and [9] and solving the resulting nonlinear equation for $\psi_s^{\text{iso}}$. To calculate the interaction between particles, the function $\sigma(\psi)$ is replaced by the straight line which is the tangent to the $\sigma(\psi)$ curve at $\psi = \psi_s^{\text{iso}}$ (Fig. 1)—this is the second ingredient of the linearized regulation model. The equation for this tangent is

$$\sigma_{\text{tangent}}(\psi) = S - K\psi. \qquad [10]$$

Thus the regulating surface is now characterized by two constants,

$$S \equiv \sigma(\psi_s^{\text{iso}}) - \psi_s^{\text{iso}}\left[\frac{\partial\sigma(\psi)}{\partial\psi}\right]_{\psi=\psi_s^{\text{iso}}}, \qquad [11]$$

$$K \equiv -\left[\frac{\partial\sigma(\psi)}{\partial\psi}\right]_{\psi=\psi_s^{\text{iso}}} \qquad [12]$$

We call the constant $K\ (\geq 0)$ the *regulation capacitance* of the surface since it has the unit of capacitance per unit area. It controls the regulation properties of the surface in that the limit $K \to \infty$ corresponds to a constant potential surface while $K \to 0$ reduces to a constant charge surface.

For an isolated planar surface adjacent to an electrolyte, the potential distribution in the electrolyte that occupies $0 < z < \infty$, obtained by solving [8], is

$$\psi(z) = \psi_s^{\text{iso}}\exp(-\kappa z), \qquad [13]$$

where

$$\psi_s^{\text{iso}} = \frac{S}{K + (\epsilon\kappa/4\pi)} \qquad [14]$$

and $(\epsilon\kappa/4\pi)$ is the diffuse layer capacitance. It is more convenient to characterize a linearized regulation surface in terms of the isolated surface potential $\psi_s^{\text{iso}}$ and the regulation capacitance $K$, rather than in terms of the original parameters $S$ and $K$ as defined in Eqs. [10] to [12].

## INTERACTING PLANAR SURFACES AND SPHERES

Given two planar charged surfaces, labelled 1 and 2, located at $z = 0$ and $h$, and separated by a layer of electrolyte characterized by Debye parameter $\kappa$, the potential distribution in $0 < z < h$ is obtained by solving [8] with boundary condition [10] at $z = 0$ and $h$,

$$\psi(z) = \frac{[\psi_2^{\text{iso}} - \Delta_2\psi_1^{\text{iso}}e^{-\kappa h}]e^{-\kappa(h-z)} + [\psi_1^{\text{iso}} - \Delta_1\psi_2^{\text{iso}}e^{-\kappa h}]e^{-\kappa z}}{1 - \Delta_1\Delta_2 e^{-2\kappa h}}, \qquad [15]$$

where

$$\Delta_i = \frac{K_i - (\epsilon\kappa/4\pi)}{K_i + (\epsilon\kappa/4\pi)}, \quad i = 1, 2, \qquad [16]$$

with $-1 \leq \Delta_i \geq 1$. $\psi_1^{\text{iso}}$ and $\psi_2^{\text{iso}}$ are the potentials of the surfaces in isolation ($h \to \infty$). The constant potential limit corresponds to $K_i \gg (\epsilon\kappa/4\pi)$, $\Delta_i \to 1$, while the constant charge limit corresponds to $K_i \ll (\epsilon\kappa/4\pi)$, $\Delta_i \to -1$. It is the relative magnitude of the regulation capacitance $K_i$ to the diffuse layer capacitance $(\epsilon\kappa/4\pi)$ that controls whether a plane surface behaves like a constant potential or a constant charge surface. For particles of other geometries, there is also a capacitance associated with the size and shape of the particle, and in such cases, we need to consider at least three competing capacitance values.

With the linear Poisson–Boltzmann equation, the force per unit area, $P(h)$, between the two surfaces due to double layer interactions is given by (2)

$$\begin{aligned} P(h) &= \frac{\epsilon}{8\pi}[\kappa^2\psi^2 - (d\psi/dz)^2] \\ &= \frac{\epsilon\kappa^2}{2\pi}\left\{\frac{2\psi_1^{\text{iso}}\psi_2^{\text{iso}}e^{-\kappa h} - [\Delta_1(\psi_2^{\text{iso}})^2 + \Delta_2(\psi_1^{\text{iso}})^2]e^{-2\kappa h}}{(1 - \Delta_1\Delta_2 e^{-2\kappa h})^2}\right. \\ &\qquad\qquad \left. - \frac{\psi_1^{\text{iso}}\psi_2^{\text{iso}}e^{-\kappa h}}{1 - \Delta_1\Delta_2 e^{-2\kappa h}}\right\}. \end{aligned} \qquad [17]$$

The interaction free energy per unit area, $F(h)$, can be found by integrating the force per unit area over the separation,

$$\begin{aligned} F(h) &= -\int_\infty^h P(x)dx \\ &= \frac{\epsilon\kappa}{4\pi}\frac{2\psi_1^{\text{iso}}\psi_2^{\text{iso}}e^{-\kappa h} - [\Delta_1(\psi_2^{\text{iso}})^2 + \Delta_2(\psi_1^{\text{iso}})^2]e^{-2\kappa h}}{1 - \Delta_1\Delta_2 e^{-2\kappa h}}. \end{aligned} \qquad [18]$$

From [17] and [18], we can recover the constant potential or constant charge limits. For instance, if the surface 1 is a constant potential surface and surface 2 is a constant charge surface, we set $\Delta_1 = 1$ and $\Delta_2 = -1$. Choosing a value of $\Delta$ between $-1$ and 1 corresponds to a linear regulation surface. For general values of the surface parameters $\Delta_1$, $\Delta_2$, $\psi_1^{\text{iso}}$, and $\psi_2^{\text{iso}}$, the interaction free energy $F(h)$ can be monotonically attractive or repulsive or exhibit a single maximum or minimum as a function of the separation $h$. This is qualitatively similar to the interaction between dissimilar nonlinear regulating surfaces (1) and the linear Debye–Hückel theory between dissimilar surfaces under constant charge or constant potential (3).

For identical surfaces, $\Delta_1 = \Delta_2 = \Delta$, $\psi_1^{\text{iso}} = \psi_2^{\text{iso}} = \psi^{\text{iso}}$, the interaction free energy per unit area simplifies to

$$F(h) = \frac{\epsilon\kappa}{2\pi}\frac{(\psi^{\text{iso}})^2e^{-\kappa h}}{1 + \Delta e^{-\kappa h}} \quad \text{(identical surfaces).} \qquad [19]$$

For $\Delta = 0$, that is, when the regulation capacitance $K$ is equal to the diffuse layer capacitance $(\epsilon\kappa/4\pi)$, we have $F(h) = (\epsilon\kappa/2\pi)(\psi^{\mathrm{iso}})^2 e^{-\kappa h}$, which is identical to the expression for the interaction free energy calculated using the linear superposition approximation. *For identical surfaces, the linear superposition approximation is exact when* $\Delta = 0$, i.e., $K = (\epsilon\kappa/4\pi)$, and for this case, the potential distribution between the plates is just the sum of the separate potential distributions due to each surface as though the surfaces are infinitely far apart [15]—the surfaces do not "sense" the presence of each other. This result explains why the linear superposition approximation appears to be so accurate in predicting the force (4) and interaction free energy (5) between spherical colloidal particles when $K = (\epsilon\kappa/4\pi)$. In this case the "negative" regulation capacitance cancels out the diffuse layer capacitance and thus renders the surfaces to be "invisible" to each other (6).

In the Deryaguin approximation, the interaction free energy between two spheres of radii $R_1$ and $R_2$ at a separation $(R_1 + R_2 + h)$ between centers is given by (7)

$$\begin{aligned} V(h) &= \frac{2\pi R_1 R_2}{R_1 + R_2}\int_h^\infty F(z)dz \\ &= \frac{\epsilon R_1 R_2}{2(R_1 + R_2)}\left[\frac{[\Delta_1(\psi_2^{\mathrm{iso}\,2} + \Delta_2(\psi_2 1^{\mathrm{iso}})^2]}{2\Delta_1\Delta_2}\ln(1 - \Delta_1\Delta_2 e^{-2\kappa h}) \right. \\ &\quad \left. + \frac{2\psi_1^{\mathrm{iso}}\psi_2^{\mathrm{iso}}}{\sqrt{|\Delta_1\Delta_2|}}\begin{Bmatrix} \arctan[(-\Delta_1\Delta_2)^{1/2}e^{-\kappa h}], (\Delta_1\Delta_2) < 0 \\ \operatorname{arctanh}[(\Delta_1\Delta_2)^{1/2}e^{-\kappa h}], (\Delta_1\Delta_2) > 0 \end{Bmatrix}\right]. \end{aligned} \quad [20]$$

## GENERAL RESULTS FOR THE INTERACTION FREE ENERGY

The interaction free energy can be found by integrating the force over separation $h$. This is numerically inefficient because many evaluations of the force as a function of separation are required to achieve good accuracy. The free energy can also be obtained directly via a thermodynamic route (8, 9). In this formulation, the free energy per unit area of formation or charging up of the two surfaces 1 and 2 has the general form

$$\mathcal{F}(h) = \left\{\int_0^{\sigma_1}\psi_1^{\mathrm{d}}d\sigma - \int_0^{\sigma_1}\psi_1^{\mathrm{s}}d\sigma\right\} + \left\{\int_0^{\sigma_2}\psi_2^{\mathrm{d}}d\sigma - \int_0^{\sigma_2}\psi_2^{\mathrm{s}}d\sigma\right\} \quad [21]$$

that is independent of any linearization assumptions. The functions $\psi_i^{\mathrm{s}}(\sigma)$ ($i = 1, 2$ for surface 1 or 2) express the surface charge density–surface potential relationship that has to be satisfied as a result of chemical reactions on each surface. For the amphoteric reaction given by Eqs. [1] and [2], the function $\psi^{\mathrm{s}}(\sigma)$ is given implicitly by [3]. For the linearized regulation model, this relation simplifies to that given by [10]. For either case, this integral involving $\psi^{\mathrm{s}}$ can be evaluated in closed form (9). For the linearized regulation model this integral is trivial. The function $\psi_i^{\mathrm{d}}(\sigma)$ is the potential on surface $i$ ($i = 1, 2$) when the surfaces are at a separation $h$ apart and it is integrated over values of the surface charge calculated according to the diffuse layer equation. For the Guoy–Chapman model one must solve the nonlinear Poisson–Boltzmann equation to determine the function $\psi_i^{\mathrm{d}}(\sigma)$. The integral cannot be evaluated in closed form in general. However, for the linear Debye–Hückel model for the diffuse layer, the expression for the surface potential on surface 1 (at $z = 0$) as a function of separation $h$, can be obtained from Eq. [15]:

$$\psi_1^{\mathrm{d}} \equiv \psi(0) = \frac{[\psi_2^{\mathrm{iso}} - \Delta_2\psi_1^{\mathrm{iso}}e^{-\kappa h}]e^{-\kappa h} + [\psi_1^{\mathrm{iso}} - \Delta_1\psi_2^{\mathrm{iso}}e^{-\kappa h}]}{1 - \Delta_1\Delta_2 e^{-2\kappa h}}. \quad [22]$$

The corresponding potential $\psi_2$ on surface 2, located at $z = h$, is obtained by interchanging 1 ↔ 2. Similarly the surface charge density on surface 1 as a function of separation is

$$\begin{aligned} \sigma_1 &= -\frac{\epsilon}{4\pi}\left[\frac{\partial\psi}{\partial z}\right]_{z=0} \\ &= \frac{\epsilon\kappa}{4\pi}\frac{[\psi_1^{\mathrm{iso}} - \Delta_1\psi_2^{\mathrm{iso}}e^{-\kappa h}] - [\psi_2^{\mathrm{iso}} - \Delta_2\psi_1^{\mathrm{iso}}e^{-\kappa h}]e^{-\kappa h}}{1 - \Delta_1\Delta_2 e^{-2\kappa h}}. \end{aligned} \quad [23]$$

The corresponding surface charge density $\sigma_2$ on surface 2, located at $z = h$, is obtained by interchanging 1 ↔ 2. Using [22] and [23] together with the corresponding equations for $\psi_2$ and $\sigma_2$ we find

$$\begin{aligned} \psi_1^{\mathrm{d}} &= \frac{4\pi}{\epsilon\kappa}\frac{\sigma_1(1 + e^{-2\kappa h}) + \sigma_2 e^{-\kappa h}}{1 + e^{-\kappa h} + e^{-2\kappa h}}, \\ \psi_2^{\mathrm{d}} &= \frac{4\pi}{\epsilon\kappa}\frac{\sigma_2(1 + e^{-2\kappa h}) + \sigma_1 e^{-\kappa h}}{1 + e^{-\kappa h} + e^{-2\kappa h}}. \end{aligned} \quad [24]$$

For the linearized Debye–Hückel model for the diffuse layer the surface potentials $\psi_1^{\mathrm{d}}$ and $\psi_2^{\mathrm{d}}$ are both linear in the surface charge density $\sigma_1$ and $\sigma_2$. Consequently by letting $\sigma_1 \to \lambda\sigma_1$ and $\sigma_2 \to \lambda\sigma_2$ and then integrating from $\lambda = 0 \to 1$, we find that the integrals in [21] become

$$\int_0^{\sigma_1}\psi_1^{\mathrm{d}}d\sigma + \int_0^{\sigma_2}\psi_2^{\mathrm{d}}d\sigma = \tfrac{1}{2}\sigma_2\psi_1 + \tfrac{1}{2}\sigma_2\psi_2. \quad [25]$$

The interaction free energy $\mathcal{V}(h)$ is found by integrating the free energy per unit area, $\mathcal{F}(h)$ [21], over the surface of each particle and subtracting the corresponding result at $h = \infty$. Thus using [25] together with [10] we get

$$\mathcal{V}(h) = \tfrac{1}{2}S_1\int(\psi - \psi^{\mathrm{iso}})dA + \tfrac{1}{2}S_2\int(\psi - \psi^{\mathrm{iso}})dA. \quad [26]$$

It is easy to verify that the result in [18] for the interaction free energy can also be derived using [22] and [26]. The interaction free energy given by this thermodynamic method is the same as that obtained by integrating the force.

For constant charge surfaces $\sigma_1 = \sigma_1^{\mathrm{iso}}$, the interaction free energy becomes

$$\mathcal{V}(h) = \tfrac{1}{2}\sigma_1^{\mathrm{iso}}\int(\psi_1 - \psi_1^{\mathrm{iso}})dA + \tfrac{1}{2}\sigma_2^{\mathrm{iso}}\int(\psi_2 - \psi_2^{\mathrm{iso}})dA, \quad [27]$$

while for constant potential surfaces, for which $\psi^{\mathrm{s}}$ is a constant ($=\psi^{\mathrm{iso}}$), we get for the interaction free energy

$$\mathcal{V}(h) = -\tfrac{1}{2}\psi_1^{\mathrm{iso}}\int(\sigma_1 - \sigma_1^{\mathrm{iso}})dA - \tfrac{1}{2}\psi_2^{\mathrm{iso}}\int(\sigma_2 - \sigma_2^{\mathrm{iso}})dA. \quad [28]$$

## NUMERICAL COMPARISONS AND CONCLUSIONS

We quantify the accuracy of the linearized regulation model for two interacting planar amphoteric surfaces characterized by Eqs. [1]–[4]. We calculate the "nonlinear" interaction free energy per unit area by solving the linearized Poisson–Boltzmann equation together with the nonlinear surface charge–surface potential relation [3]. These results are compared with those obtained with the linearized Poisson–Boltzmann equation together with the linearized regulation model based on Eqs. [10]–[12]. In Figs. 2, we show the relative error defined by

$$\text{relative error} = \frac{\text{"nonlinear"} - \text{"linear"}}{\text{"nonlinear"}} \times 100\%$$

as a function of $\Delta\mathrm{p}K \equiv (\mathrm{p}K_- - \mathrm{p}K_+)$ for various system parameters. We have set

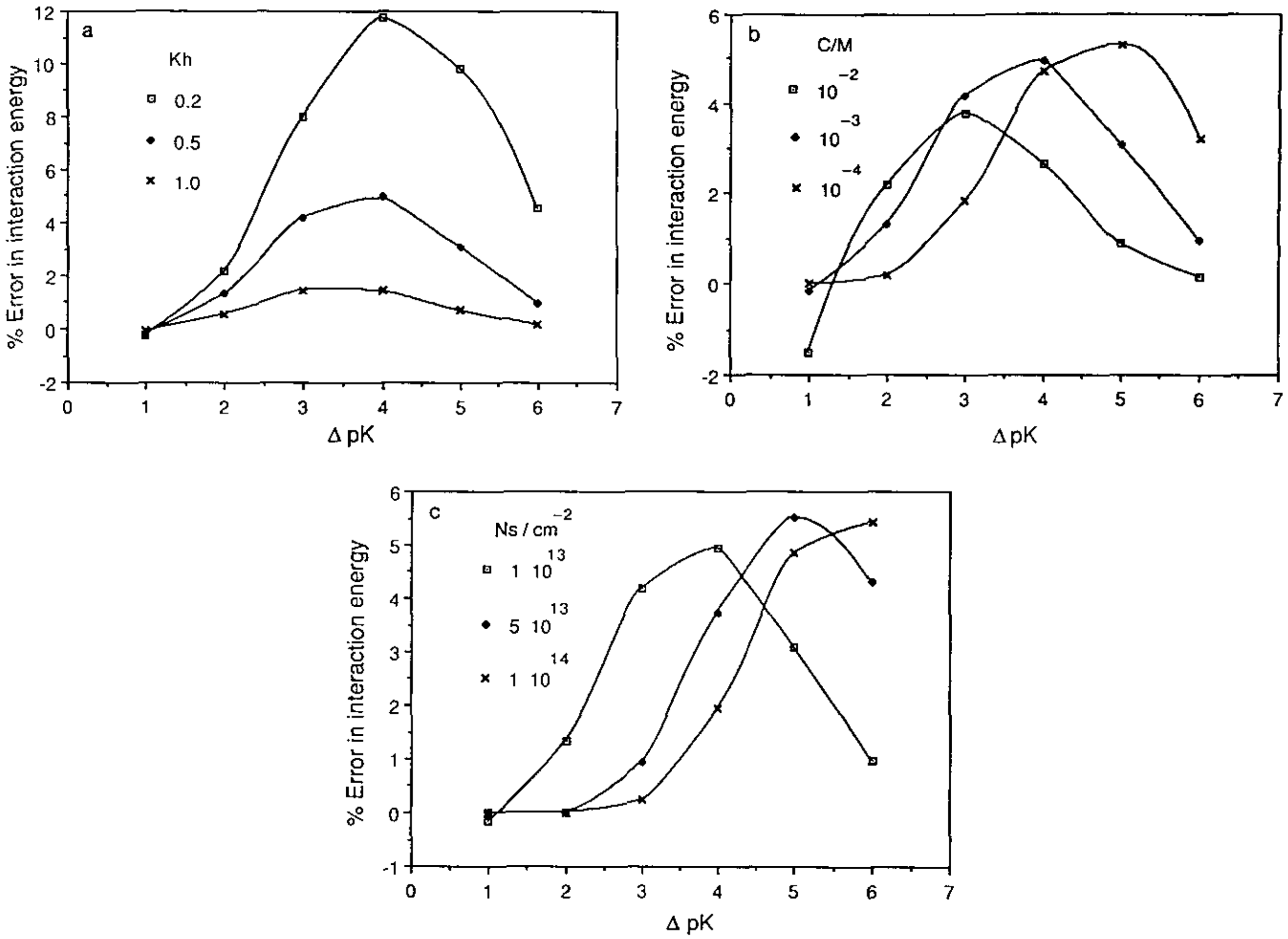

FIG. 2. Variations of the relative error in the interaction free energy between planar amphoteric surfaces with $\Delta pK$: (a) for varying $\kappa h$ (the 1:1 electrolyte concentration is $10^{-3} M$, the surface site density $N_s$ is $1.0 \times 10^{13}$ cm$^{-2}$); (b) for varying electrolyte concentration ($\kappa h$ is fixed at 0.5, the surface site density $N_s$ is $1.0 \times 10^{13}$ cm$^{-2}$); (c) for varying surface site density $N_s$ (the 1:1 electrolyte concentration is $10^{-3} M$, the surface separation $\kappa h$ is fixed at 0.5). $[\frac{1}{2}(pK_+ + pK_-) - \text{pH}]$ is fixed at $-1$ for all cases.

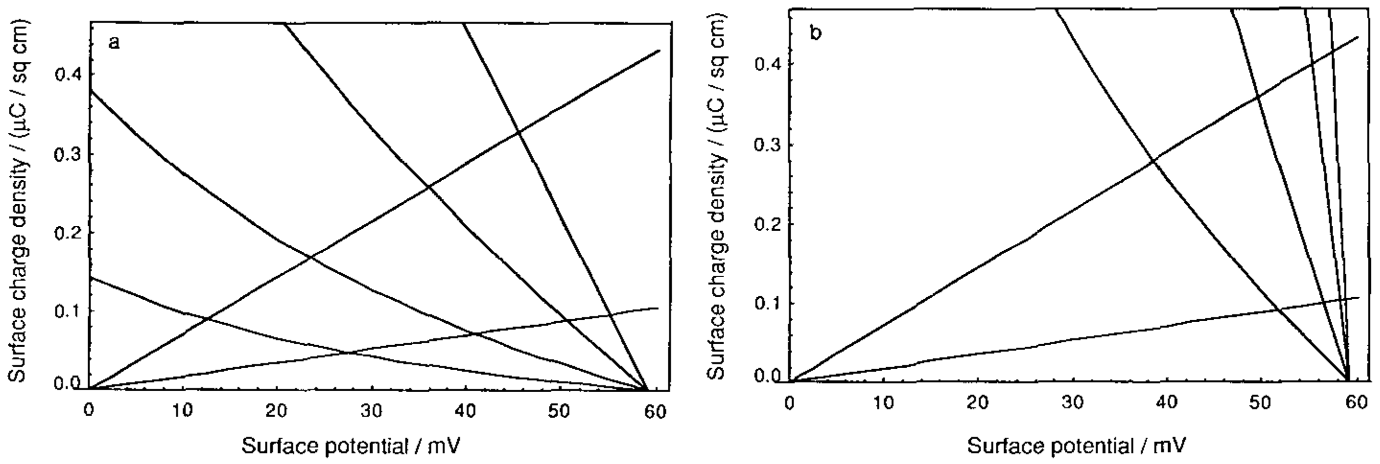

FIG. 3. The charge–potential curves for two identical amphoteric surfaces at separation $\kappa h = 0.5$, $10^{-3} M$ 1:1 electrolyte concentration, $\Delta pK = 1, 2, 3$, and 4, and surface site density $N_s$ equal to (a) $1.0 \times 10^{13}$ cm$^{-2}$ and (b) $1.0 \times 10^{14}$ cm$^{-2}$.

$$\Delta pH = [\tfrac{1}{2}(pK_+ + pK_-) - pH] = -1$$

so that the magnitude of the surface potential of an isolated surface is no higher than 59 mV and the use of the linearized Poisson–Boltzmann (Debye–Hückel) equation is expected to be accurate.

By using the linear Poisson–Boltzmann equation in both calculations we are concentrating on the error due to the use of the tangent line, equation [10] (the linearized regulation approximation), to approximate the nonlinear amphoteric charge–potential relation given in Equation [3]. This error depends on the curvature of the charge–potential curve which in turn depends on the interplay between the values of $\Delta pK$, the separation $\kappa h$, and the surface site density $N_s$. The error is expected to be larger at smaller separations since the linearized regulation (tangent line) approximation for the amphoteric charge–potential curve is most accurate in the neighborhood of $\psi^{\text{iso}}$ (see Fig. 2a). At a fixed separation, the error is large when the curvature in the amphoteric charge–potential curve becomes significant. For example, the movement of the position of large relative error to higher $\Delta pK$ values seen in Fig. 2c can be understood in terms of the data given in Fig. 3, where we see that when the site density $N_s$ increases from $1.0 \times 10^{13}$ cm$^{-2}$ to $1.0 \times 10^{14}$ cm$^{-2}$, the region of the amphoteric charge–potential curve that becomes significantly nonlinear moves to larger $\Delta pK$ values. We have performed similar calculations for the case of two identical spherical particles—in that case, the relative error is even lower than those shown in Figs. 2a–c for the same distance of closest approach. This is reasonable because this geometry involves interaction between surface elements that are further apart than the distance of closest approach and therefore have lower error.

It has been established that the linearized Poisson–Boltzmann (Debye–Hückel) equation is adequate for describing the double layer interaction between colloidal particles at low to modest surface potentials. The linearized regulation approximation introduced here provides a consistent treatment for handling the interaction between surfaces that exhibit charge regulation. These observations allow us to use this approximate theory to determine the interaction between colloidal particles of other geometries, not just planar surfaces. Although some numerical effort is required to make progress in this direction, the effort involved in dealing with the linearized Poisson–Boltzmann (Debye–Hückel) equation is considerably less than that required to solve the full nonlinear Poisson–Boltzmann equation (10).

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