JOURNAL OF COLLOID AND INTERFACE SCIENCE **198,** 42–52 (1998)
ARTICLE NO. CS975240

Electrostatic Interaction between a Sphere and a Planar Surface: Generalization of Point-Charge/Surface Image Interaction to Particle/Surface Image Interaction

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Received June 26, 1997; accepted October 17, 1997

An explicit exact analytic expression for the energy of the electrostatic interaction between a platelike particle 1 and a spherical particle 2 of radius a_2 immersed in an electrolyte solution of Debye–Hückel parameter κ is derived on the basis of the linearized Poisson–Boltzmann equation. Both particles may have either constant surface potential or constant surface charge density. In the limit of $\kappa a_2 \to 0$, the interaction between a plate with zero surface charge density and a sphere having constant surface charge density becomes identical to the usual image interaction between a point charge and an uncharged plate. The present theory thus leads to a generalization of the usual image interaction of a point charge to cover the case of a charged colloidal particle of finite size.

Key Words: **sphere/surface interaction; electrostatic interaction; image interaction.**

1. INTRODUCTION

Electrostatic interactions between charged colloidal particles play an essential role in determining the behavior of colloidal suspensions (1, 2). In order to calculate the potential energy of electrostatic interactions, one needs to solve the Poisson–Boltzmann equation for the electric potential distribution in the system of interacting particles. Recently we have shown (3–11) that the linearized Poisson–Boltzmann equation (the Debye–Hückel equation) can exactly be solved for two interacting charged spherical particles for various types of boundary conditions at the surfaces of interacting particles. On the basis of the obtained potential distribution, we have derived explicit exact analytic expressions for the interaction energy for these systems without recourse

The electrostatic interaction between two spheres of considerably different sizes can be approximated as the plate/sphere interaction. The electrostatic interaction between a plate and a sphere is thus of particular interest (17–22, 4, 8). Interactions of this type are also quite often encountered in practical situations, such as collection of colloidal particles at the surface of flat substrates.

Because of mathematical difficulties, however, it is not easy to derive an interaction energy expression between a plate and a sphere from the expressions obtained in our previous papers (6, 9, 10[1]) for the interaction energy between two spheres of radii a_1 and a_2 by taking the limit $a_2 \to \infty$, since the spherical polar coordinate is used for both spheres. In the present paper, the cylindrical coordinate and the spherical coordinate are both used. We also elucidate how the image interaction of a charged colloidal particle with a plate is related to the usual image interaction of a point charge with a plate.

2. INTERACTION BETWEEN A PLATE AND A SPHERE, BOTH AT CONSTANT SURFACE POTENTIAL

2.1. Linearized Poisson–Boltzmann Equation

Consider a hard plate (of semi-infinite thickness) carrying a constant surface potential ψ_{01} (plate 1) and a charged hard sphere of radius a_2 carrying a constant surface potential ψ_{02} (sphere 2), separated by a distance H between their surfaces, immersed in an electrolyte solution. We employ both a cylindrical coordinate system (s, ϕ, z) and a spherical polar coordinate system (r, θ, ϕ), as shown in Fig. 1, in which the origin of the cylindrical coordinate system, O_1, is located

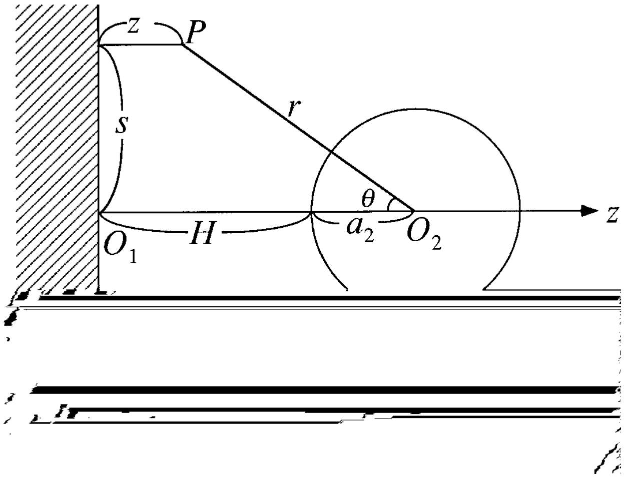

FIG. 1. Interaction between a charged ion-impenetrable hard plate (plate 1) and a hard sphere (sphere 2) of radius a_2 at a separation H between their surfaces.

the z-axis (the line O_1O_2), which is perpendicular to the surface of plate 1, and ϕ is the azimuthal angle about the z-axis. We first treat the case where the surface potentials of plate 1 and sphere 2 both remain constant during interaction independent of H.

We assume that the electric potential ψ at any point in the solution phase, measured relative to the bulk solution phase (where ψ is set equal to zero), is low enough to obey the following linearized Poisson–Boltzmann equation, viz.,

$$\Delta\psi = \kappa^2\psi, \qquad [2.1]$$

where κ is the Debye–Hückel parameter of the electrolyte solution. As a result of symmetry of the system, the potential ψ does not depend on the azimuthal angle ϕ so that ψ is a function of s and z, i.e. $\psi = \psi(s, z)$, or a function of r and θ, i.e. $\psi = \psi(r, \theta)$. The boundary conditions for ψ are

$$\psi(s, 0) = \psi_{o1} \quad \text{constant (on plate 1)}, \qquad [2.2]$$

$$\psi(a_2, \theta) = \psi_{o2} \quad \text{constant (on sphere 2)}. \qquad [2.3]$$

We can write the solution to Eq. [2.1] subject to the boundary conditions [2.2] and [2.3] in the following form (Fig. 2):

$$\begin{aligned}\psi = \psi_1^{(0)} + \psi_2^{(0)} + [\psi_1^{(1)} + \psi_1^{(2)} + \psi_1^{(3)} + \cdots \\ + \psi_1^{(2n)} + \psi_1^{(2n+1)} + \cdots] + [\psi_2^{(1)} + \psi_2^{(2)} \\ + \psi_2^{(3)} + \cdots + \psi_2^{(2n)} + \psi_2^{(2n+1)} + \cdots]. \qquad [2.4]\end{aligned}$$

As will be shown below, the kth-order term $\psi_i^{(k)}$ can be obtained by the method of images from the (k–1)-order term $\psi_i^{(k-1)}$ ($k = 1, 2, \cdots$ and $i = 1, 2$), and it is essential that each $\psi_i^{(k)}$ is expressed both in the (r, θ) and (s, z) coordinate systems.

2.2. Zeroth-Order Terms

As the zeroth-order terms $\psi_1^{(0)}(r_1)$ and $\psi_2^{(0)}(r_2)$, we choose the unperturbed potentials produced by plate 1 and sphere 2 in the absence of interaction (that is, when they are isolated at infinite H), which are functions of only z and r, respectively, viz.,

$$\psi_1^{(0)}(z) = \psi_{o1}\exp(-\kappa z), \quad z \geq 0, \qquad [2.5]$$

$$\psi_2^{(0)}(r) = \psi_{o2}\frac{a_2}{r}\exp[-\kappa(r - a_2)], \quad r \geq a_2. \qquad [2.6]$$

Note that $\psi_1^{(0)}(z)$ and $\psi_2^{(0)}(r)$, respectively, satisfy the

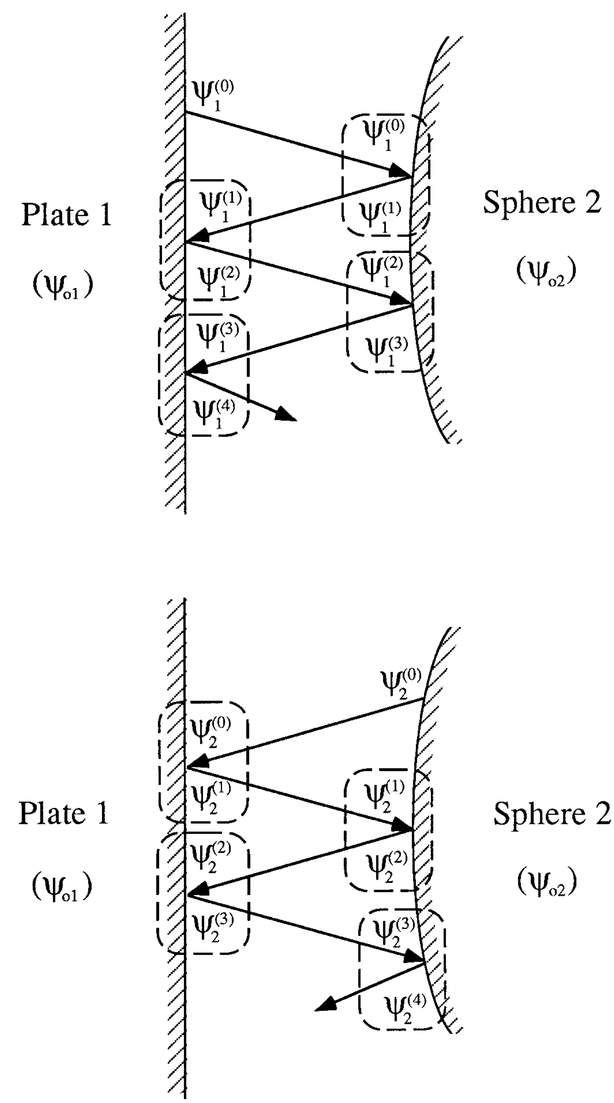

FIG. 2. The unperturbed potentials $\psi_1^{(0)}$, $\psi_2^{(0)}$, and the correction terms $\psi_1^{(k)}$ and $\psi_2^{(k)}$ ($k = 1, 2, \cdots$) for the constant surface potential case (see also Ref. (6)).

boundary conditions [2.2] and [2.3]. In order to obtain $\psi_1^{(k)}$ and $\psi_2^{(k)}$ ($k \geq 1$), it is convenient to derive an alternative expression for $\psi_1^{(0)}(z)$ (or $\psi_2^{(0)}(r)$) on the basis of the (r, θ) (or (s, z)) coordinate system, viz.,

$$\psi_1^{(0)}(r, \theta) = \psi_{01} e^{-\kappa(H+a_2)} \sqrt{\frac{\pi}{2\kappa}} \times \sum_{n=0}^{\infty} (2n+1) \frac{I_{n+1/2}(\kappa r)}{\sqrt{r}} P_n(\cos\theta), \quad [2.7]$$

$$\psi_2^{(0)}(s, z) = \psi_{02} a_2 e^{\kappa a_2} \times \int_0^{\infty} \frac{\exp[-\sqrt{k^2+\kappa^2}\,(H+a_2-z)]}{\sqrt{k^2+\kappa^2}} J_0(ks) k\,dk, \quad [2.8]$$

where $I_{n+1/2}(x)$ and $J_0(x)$ are, respectively, the modified Bessel function of the first kind and the zero-order ordinal Bessel function, and we have used the following formulas (23):

$$\exp(\kappa r \cos\theta) = \sqrt{\frac{\pi}{2\kappa}} \sum_{n=0}^{\infty} (2n+1) \times \frac{I_{n+1/2}(\kappa r)}{\sqrt{r}} P_n(\cos\theta), \quad [2.9]$$

$$\frac{\exp(-\kappa r)}{r} = \int_0^{\infty} \frac{\exp[-\sqrt{k^2+\kappa^2}\, r\cos\theta]}{\sqrt{k^2+\kappa^2}} J_0(kr\sin\theta) k\,dk, \quad [2.10]$$

which lead to Eqs. [2.7] and [2.8], respectively, if one sets $r\sin\theta = s$ and $r\cos\theta = H + a_2 - z$.

2.3. First-Order Terms

We construct the first-order terms $\psi_1^{(1)}$ and $\psi_2^{(1)}$ as follows. First we start with the unperturbed potential $\psi_1^{(0)}(z)$, which satisfies the boundary condition [2.2] on plate 1. The boundary condition [2.3] on sphere 2, on the other hand, which has been satisfied already by $\psi_2^{(0)}(r)$, is now violated, since $\psi_1^{(0)}(z)$ gives rise to the following nonzero value on sphere 2:

$$\psi_1^{(0)}(a_2, \theta) = \psi_{01} e^{-\kappa(H+a_2)} \sqrt{\frac{\pi}{2\kappa}} \times \sum_{n=0}^{\infty} (2n+1) \frac{I_{n+1/2}(\kappa a_2)}{\sqrt{a_2}} P_n(\cos\theta), \quad [2.11]$$

which is obtained from Eq. [2.7]. We thus construct the first-order term $\psi_1^{(1)}$ so as to cancel $\psi_1^{(0)}(a_2, \theta)$ on sphere 2, viz.,

$$\psi_1^{(0)}(a_2, \theta) + \psi_1^{(1)}(a_2, \theta) = 0 \quad \text{(on sphere 2)}. \quad [2.12]$$

Therefore, $\psi_1^{(1)}$ must take the form

$$\psi_1^{(1)}(r, \theta) = \psi_{01} e^{-\kappa(H+a_2)} \sqrt{\frac{\pi}{2\kappa}} \sum_{n=0}^{\infty} (2n+1) \times G_n(2) \frac{K_{n+1/2}(\kappa r)}{\sqrt{r}} P_n(\cos\theta), \quad [2.13]$$

where

$$G_n(2) = -\frac{I_{n+1/2}(\kappa a_2)}{K_{n+1/2}(\kappa a_2)}. \quad [2.14]$$

Equation [2.12] can be rewritten on the basis of the (s, z) coordinate system, viz.,

$$\psi_1^{(1)}(s, z) = \psi_{01} e^{-\kappa(H+a_2)} \frac{\pi}{2\kappa} \times \int_0^{\infty} \frac{\exp[-\sqrt{k^2+\kappa^2}(H+a_2-z)]}{\sqrt{k^2+\kappa^2}} \sum_{n=0}^{\infty} (2n+1) \times G_n(2) P_n\left(\frac{\sqrt{k^2+\kappa^2}}{\kappa}\right) J_0(ks) k\,dk. \quad [2.15]$$

Here we have used the following formula:

$$\frac{K_{n+1/2}(\kappa r)}{\sqrt{r}} P_n(\cos\theta) = \sqrt{\frac{\pi}{2\kappa}} \int_0^{\infty} \times \frac{\exp[-\sqrt{k^2+\kappa^2}\, r\cos\theta]}{\sqrt{k^2+\kappa^2}} \times P_n\left(\frac{\sqrt{k^2+\kappa^2}}{\kappa}\right) J_0(kr\sin\theta) k\,dk, \quad [2.16]$$

which leads to Eq. [2.15], if one sets $r\sin\theta = s$ and $r\cos\theta = H + a_2 - z$.

We now start with the unperturbed potential $\psi_2^{(0)}(r)$, which satisfies the boundary condition [2.3] on sphere 2. The boundary condition [2.2] on plate 1, on the other hand, which has been satisfied already by $\psi_1^{(0)}(z)$, is now violated, since $\psi_2^{(0)}(z)$ gives rise to a nonzero value on sphere 2. We thus construct the first-order term $\psi_2^{(1)}$ so as to cancel $\psi_2^{(0)}(s, 0)$ on plate 1, viz.,

$$\psi_2^{(0)}(s, 0) + \psi_2^{(1)}(s, 0) = 0 \quad \text{(on plate 1)}. \quad [2.17]$$

Therefore, $c_1^{(1)}$ must take the form

$$c_2^{(1)}(s, z) \quad 0\, c_{02} a_2 e^{k a_2}$$
$$1 \int_0^\infty \frac{\exp[0\sqrt{k^2 / k^2}(H / a_2 \; 0 \; z)]}{\sqrt{k^2 / k^2}} J_0(ks)kdk, \quad [2.18]$$

which can be rewritten in the (r, u) coordinate system as

$$c_2^{(1)}(r, u) \quad 0\, c_{02} a_2 \sqrt{\frac{2k}{p}}\, e^{k a_2} \sum_{n \; 0}^{\infty} (2n / 1)$$
$$1\; b_{n0} \frac{I_{n/1/2}(kr)}{\sqrt{r}} P_n(\cos u). \quad [2.19]$$

2.4. Second- and Higher Order Terms

In a similar way, we can construct the second-order terms $c_1^{(2)}$ and $c_2^{(2)}$ so as to cancel $c_1^{(1)}$ on plate 1 and $c_2^{(1)}$ on sphere 2, respectively, viz.,

$$c_1^{(1)}(s, 0) \; / \; c_1^{(2)}(s, 0) \quad 0 \quad (\text{on plate } 1), \quad [2.20]$$
$$c_2^{(1)}(a_2, u) \; / \; c_2^{(2)}(a_2, u) \quad 0 \quad (\text{on sphere } 2). \quad [2.21]$$

Thus $c_1^{(2)}$ is given by

$$c_1^{(2)}(s, z) \quad 0\, c_{01} e^{0\, k(H/a_2)} \frac{p}{2k}$$
$$1 \int_0^\infty \frac{\exp[0\sqrt{k^2 / k^2}(H / a_2 / z)]}{\sqrt{k^2 / k^2}} \sum_{n \; 0}^{\infty} (2n / 1)$$
$$1\; G_n(2) P_n\left(\frac{\sqrt{k^2 / k^2}}{k}\right) J_0(ks)kdk. \quad [2.22]$$

Equation [2.22] can be rewritten in the (r, u) coordinate system as

$$c_1^{(2)}(r, u) \quad 0\, c_{01} e^{0\, k(H/a_2)} \sqrt{\frac{p}{2k}} \sum_{n \; 0}^{\infty} \sum_{m \; 0}^{\infty}$$
$$1\; (2n / 1)(2m / 1) b_{nm}$$
$$1\; G_n(2) \frac{I_{m/1/2}(kr)}{\sqrt{r}} P_m(\cos u), \quad [2.23]$$

where

$$b_{nm} \quad \frac{p}{2k} \int_0^\infty \frac{\exp[0\, 2\sqrt{k^2 / k^2}(H / a_2)]}{\sqrt{k^2 / k^2}}$$
$$1\; P_n\left(\frac{\sqrt{k^2 / k^2}}{k}\right) P_m\left(\frac{\sqrt{k^2 / k^2}}{k}\right) kdk$$
$$\frac{p}{2} \int_1^\infty e^{0\, 2kt(H/a_2)} P_n(t) P_m(t) dt. \quad [2.24]$$

Or, alternatively (24–26),

$$b_{nm} \quad \sum_{r \; 0}^{\min\{n,m\}} A_{nmr} \sqrt{\frac{p}{4k(H / a_2)}} K_{n/m\,0\,2r/1/2}(2k(H / a_2)), \quad [2.25]$$

where

$$A_{nmr} \quad [G(n \; 0 \; r / \tfrac{1}{2}) G(m \; 0 \; r / \tfrac{1}{2})$$
$$1\; G(r / \tfrac{1}{2})(n / m \; 0 \; r)!(n / m \; 0 \; 2r / \tfrac{1}{2})]/$$
$$[pG(m / n \; 0 \; r / \tfrac{3}{2})(n \; 0 \; r)!(m \; 0 \; r)!r!]. \quad [2.26]$$

For the special case where $n \quad 0$ or $m \quad 0$,

$$b_{n0} \quad b_{0n} \quad \frac{p}{2} \int_1^\infty e^{0\, 2kt(H/a_2)} P_n(t) dt$$
$$\sqrt{\frac{p}{4k(H / a_2)}} K_{n/1/2}(2k(H / a_2)), \quad [2.27]$$

and for $n \quad m \quad 0$,

$$b_{00} \quad \frac{p}{4k(H / a_2)} e^{0\, 2k(H/a_2)}. \quad [2.28]$$

Similarly, we obtain for $c_2^{(2)}$

$$c_2^{(2)}(r, u) \quad 0\, c_{02} a_2 e^{k a_2} \sqrt{\frac{2k}{p}} \sum_{n \; 0}^{\infty} (2n / 1)$$
$$1\; b_{n0} G_n(2) \frac{K_{n/1/2}}{\sqrt{r}} P_n(\cos u) \quad [2.29]$$

By repeating the above procedure one can construct $c_1^{(2n\,0\,2)}$, $c_1^{(2n\,0\,1)}$, $c_2^{(2n\,0\,2)}$, and $c_2^{(2n\,0\,1)}$ (n 1, 2, · · ·) that satisfy

$$c_1^{(2n\,0\,1)}(s, 0) \; / \; c_1^{(2n)}(s, 0) \quad 0 \; (\text{on plate } 1), \quad [2.30]$$
$$c_1^{(2n\,0\,2)}(a_2, u) \; / \; c_1^{(2n\,0\,1)}(a_2, u) \quad 0 \; (\text{on sphere } 2), \quad [2.31]$$
$$c_2^{(2n\,0\,2)}(s, 0) \; / \; c_2^{(2n\,0\,1)}(s, 0) \quad 0 \; (\text{on plate } 1), \quad [2.32]$$
$$c_2^{(2n\,0\,1)}(a_2, u) \; / \; c_2^{(2n)}(a_2, u) \quad 0 \; (\text{on sphere } 2), \quad [2.33]$$

so that the boundary conditions [2.2] and [2.3] are satisfied, viz.,

$$c(0, s) \quad c_1^{(0)}(0) \; / \sum_{n \; 1}^{\infty} [c_1^{(2n\,0\,1)}(s, 0) \; / \; c_1^{(2n)}(s, 0)]$$
$$/ \sum_{n \; 1}^{\infty} [c_2^{(2n\,0\,2)}(s, 0) \; / \; c_2^{(2n\,0\,1)}(s, 0)]$$
$$c_{01}, \quad (\text{on plate } 1), \quad [2.34]$$

$$\psi(a,\theta) = \psi_2^{(0)}(a) + \sum_{n=1}^{\infty}\left[\psi_1^{(2n-2)}(a,\theta) + \psi_1^{(2n-1)}(a,\theta)\right] + \sum_{n=1}^{\infty}\left[\psi_2^{(2n-1)}(a,\theta) + \psi_2^{(2n)}(a,\theta)\right] = \psi_{02} \quad \text{(on sphere 2).} \qquad [2.35]$$

2.5. Potential Energy of Electrostatic Interaction

The free energy $F(H)$ of the present system can be obtained by applying a method of Verwey and Overbeek (1). In the case of low potentials $F(H)$ is given by

$$F(H) = -\frac{1}{2}\int_{S_1} \sigma_1 \psi_{01}\, dS_1 - \frac{1}{2}\int_{S_2} \sigma_2 \psi_{01}\, dS_2 = -\frac{1}{2}\psi_{01}\int_0^{\infty} \sigma_2(s) 2\pi s\, ds - \frac{1}{2}\psi_{02}\int_0^{\pi} \sigma_1(\theta_1) 2\pi a^2 \sin\theta\, d\theta, \qquad [2.36]$$

where the integral is carried out over the surface S_1 of plate 1 and the surface S_2 of sphere 2. The surface charge densities σ_1 on plate 1 and σ_2 on sphere 2 are related to the potential derivative at their surfaces as

$$\sigma_1(s) = -\varepsilon\varepsilon_0 \left.\frac{\partial \psi}{\partial z}\right|_{z=0^+}, \qquad [2.37]$$

$$\sigma_2(\theta_2) = -\varepsilon\varepsilon_0 \left.\frac{\partial \psi}{\partial r}\right|_{r=a_2^+}, \qquad [2.38]$$

where ε is the relative permittivity of the electrolyte solution and ε_0 is the permittivity of a vacuum. Substituting the obtained expressions for the potential distribution into Eq. [2.36], we obtain the required result for the interaction energy between plate 1 and sphere 2 at constant surface potential, viz.,

$$\begin{aligned}
V(H) = {} & 4\pi\varepsilon\varepsilon_0\psi_{01}\psi_{02}a_2 e^{-\kappa H} + \pi^2\varepsilon\varepsilon_0\psi_{01}^2 \frac{1}{\kappa} e^{-2\kappa(H+a_2)} \\
& \times \sum_{n=0}^{\infty}(2n+1)G_n(2) - 4\varepsilon\varepsilon_0\psi_{02}^2\kappa a_2^2 e^{2\kappa a_2}\beta_{00} \\
& - 2\pi\varepsilon\varepsilon_0\psi_{01}\psi_{02}a_2 e^{-\kappa H}\sum_{n=0}^{\infty}(2n+1)(\beta_{0n}+\beta_{n0}) \\
& \times G_n(2) - \pi^2\varepsilon\varepsilon_0\psi_{01}^2\frac{1}{\kappa}\psi_{02}e^{-2\kappa(H+a_2)}\sum_{n=0}^{\infty}\sum_{m=0}^{\infty} \\
& \times (2n+1)(2m+1)\beta_{nm}G_n(2)G_m(2) \\
& + 4\varepsilon\varepsilon_0\psi_{02}^2\kappa a_2^2 e^{2\kappa a_2}\sum_{n=0}^{\infty}(2n+1)\beta_{0n}\beta_{n0}G_n(2) \\
& + 2\pi\varepsilon\varepsilon_0\psi_{01}\psi_{02}a_2 e^{-\kappa H}\sum_{n=0}^{\infty}\sum_{m=0}^{\infty} \\
& \times (2n+1)(2m+1)\beta_{nm}(\beta_{0n}+\beta_{m0}) \\
& \times G_n(2)G_m(2) + \cdots - 2\pi\varepsilon\varepsilon_0\psi_{01}\psi_{02}a_2 e^{-\kappa H} \\
& \times \sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\cdots\sum_{n_\nu=0}^{\infty}(-1)^{\nu-1} \\
& \times (2n_1+1)(2n_2+1)\cdots(2n_\nu+1) \\
& \times \beta_{n_1n_2}\beta_{n_2n_3}\cdots\beta_{n_{\nu-1}n_\nu}(\beta_{0n_1}+\beta_{n_\nu 0})G_{n_1}(2) \\
& \times G_{n_2}(2)\cdots G_{n_\nu}(2) + \pi^2\varepsilon\varepsilon_0\psi_{01}^2\frac{1}{\kappa}e^{-2\kappa(H+a_2)} \\
& \times \sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\cdots\sum_{n_\nu=0}^{\infty}(-1)^{\nu-1}(2n_1+1) \\
& \times (2n_2+1)\cdots(2n_\nu+1)\beta_{n_1n_2}\beta_{n_2n_3}\cdots\beta_{n_{\nu-1}n_\nu} \\
& \times G_{n_1}(2)G_{n_2}(2)\cdots G_{n_\nu}(2) + 4\varepsilon\varepsilon_0\psi_{02}^2\kappa a_2^2 e^{2\kappa a_2} \\
& \times \sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\cdots\sum_{n_\nu=0}^{\infty}(-1)^{\nu-1} \\
& \times (2n_1+1)(2n_2+1)\cdots(2n_\nu+1) \\
& \times \beta_{n_1n_2}\beta_{n_2n_3}\cdots\beta_{n_{\nu-1}n_\nu}\beta_{0n_1}\beta_{n_\nu 0} \\
& \times G_{n_1}(2)G_{n_2}(2)\cdots G_{n_\nu}(2) + \cdots
\end{aligned} \qquad [2.39]$$

3. INTERACTION BETWEEN A PLATE AND A SPHERE, BOTH AT CONSTANT SURFACE CHARGE DENSITY

We next consider the case where the surface charge densities of plate 1 and sphere 2 remain constant. In this case one must take into account the electric fields induced within the interacting particles. The Laplace equations for the internal regions of plate 1 and sphere 2 as well as the linearized Poisson–Boltzmann equations for the outside of plate 1 and sphere 2 must be considered:

$$\Delta\psi = \kappa^2\psi, \quad \text{outside plate 1 and sphere 2,} \qquad [3.1]$$

$$\Delta\psi_{\text{in}1} = 0, \quad \text{inside plate 1,} \qquad [3.2]$$

$$\Delta\psi_{\text{in}2} = 0, \quad \text{inside sphere 2.} \qquad [3.3]$$

The boundary conditions for ψ, $\psi_{\text{in}1}$, and $\psi_{\text{in}2}$ are thus

$$\psi_{\text{in}1}(s, 0^-) = \psi(s, 0^+), \qquad [3.4]$$

$$\varepsilon_1 \left.\frac{\partial \psi_{\text{in}1}}{\partial z}\right|_{z=0^-} - \varepsilon \left.\frac{\partial \psi}{\partial z}\right|_{z=0^+} = \frac{\sigma_1}{\varepsilon_0}, \qquad [3.5]$$

at the surface of plate 1, and

$$\psi_{\text{in}2}(a_2^-, \theta) = \psi(a_2^+, \theta), \qquad [3.6]$$

$$\varepsilon_2 \left.\frac{\partial \psi_{\text{in}2}}{\partial r}\right|_{r=a_2^-} - \varepsilon \left.\frac{\partial \psi}{\partial r}\right|_{r=a_2^+} = \frac{\sigma_2}{\varepsilon_0}, \qquad [3.7]$$

at the surface of sphere 2. Here ε_1 and ε_2 are, respectively, the relative permittivities of plate 1 and sphere 2, and the

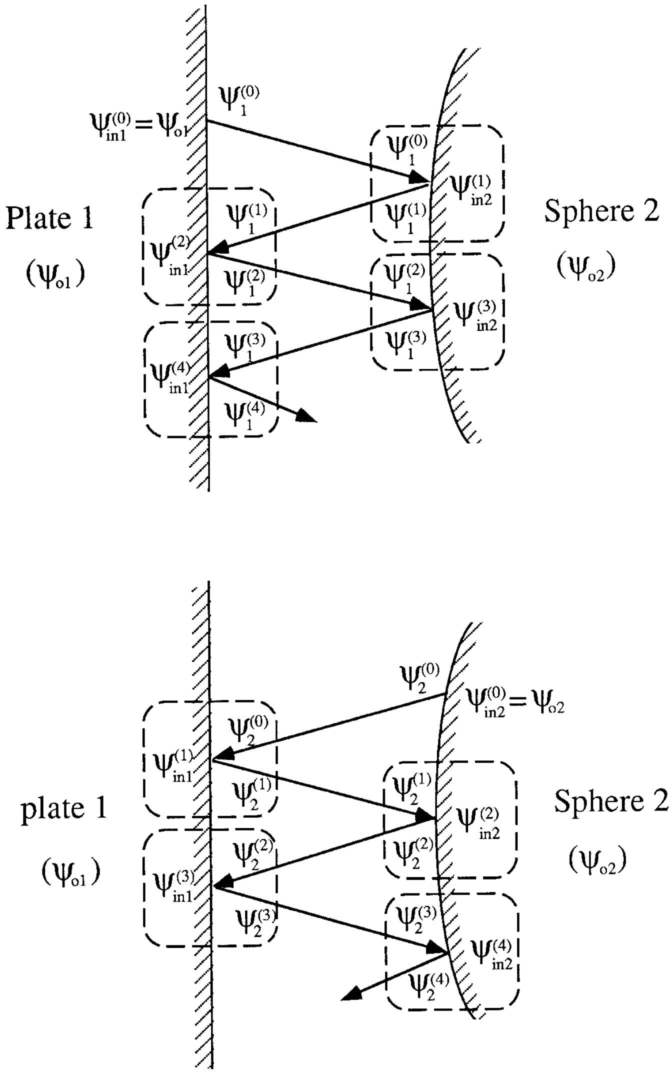

FIG. 3. The unperturbed potentials $c_1^{(0)}$, $c_2^{(0)}$, $c_{in1}^{(0)}$, and $c_{in2}^{(0)}$ and the correction terms $c_1^{(k)}$, $c_2^{(k)}$, $c_{in1}^{(k)}$, and $c_{in2}^{(k)}$ (k 1, 2, $\cdots$) for the constant surface charge density case (see also Ref. (9)).

unperturbed surface potentials c_{01} and c_{02} are related to the surface charge densities s_1 of plate 1 and s_2 of sphere 2 by

$$s_1 \quad ee_0 k c_{01}, \qquad [3.8]$$

$$s_2 \quad ee_0 k c_{02}\left(1 \; / \; \frac{1}{ka_2}\right). \qquad [3.9]$$

We can write the solution to Eqs. [3.1]–[3.3] subject to the boundary conditions [3.4]–[3.7] in the following form (Fig. 3):

$$c \quad c_1^{(0)} \; / \; c_2^{(0)} \; / \; [c_1^{(1)} \; / \; c_1^{(2)} \; / \; c_1^{(3)} \; / \; \cdots]$$
$$/ \; [c_2^{(1)} \; / \; c_2^{(2)} \; / \; c_2^{(3)} \; / \; \cdots],$$
$$\text{outside plate 1 and sphere 2,} \qquad [3.10]$$

$$c_{in1} \quad c_{in1}^{(0)} \; / \; c_{in1}^{(1)} \; / \; c_{in1}^{(2)} \; / \; c_{in1}^{(3)} \; / \; \cdots, \quad \text{inside plate 1,} \qquad [3.11]$$

$$c_{in2} \quad c_{in2}^{(0)} \; / \; c_{in2}^{(1)} \; / \; c_{in2}^{(2)} \; / \; c_{in2}^{(3)} \; / \; \cdots, \quad \text{inside sphere 2.} \qquad [3.12]$$

As the zeroth-order terms $c_1^{(0)}$, $c_2^{(0)}$, $c_{in}^{(0)}$, and $c_{in2}^{(0)}$, we choose the unperturbed potentials produced by plate 1 and sphere 2 when they are isolated,

$$c_1^{(0)}(z) \quad c_{01}\exp(0\,kz), \quad z \; ¢ \; 0, \qquad [3.13]$$

$$c_2^{(0)}(r) \quad c_{02}\,\frac{a_2}{r}\exp[0\,k(r\;0\;a_2)], \quad r \; ¢ \; a_2, \qquad [3.14]$$

$$c_{in1}^{(0)}(z) \quad c_{01}, \quad z \; ¡ \; 0, \qquad [3.15]$$

$$c_{in2}^{(0)}(r) \quad c_{02}, \quad 0 \; ¡ \; r \; ¡ \; a_2, \qquad [3.16]$$

which satisfy the following boundary conditions:

$$0\,e\,\frac{í c_1^{(0)}}{í z}\bigg|_{z\;0^/} \quad \frac{s_1}{e_0}, \qquad [3.17]$$

$$0\,e\,\frac{í c_2^{(0)}}{í r}\bigg|_{r\;a^/} \quad \frac{s_2}{e_0}, \qquad [3.18]$$

$$c_{in1}^{(0)}(0^0) \quad c_1^{(0)}(0^/) \quad c_{01}, \qquad [3.19]$$

$$c_{in2}^{(0)}(a^0) \quad c_2^{(0)}(a^/) \quad c_{02}. \qquad [3.20]$$

The first- and higher order terms $c_1^{(2n)}$, $c_1^{(2n01)}$, $c_2^{(2n)}$, $c_2^{(2n01)}$, $c_{in1}^{(2n)}$, $c_{in1}^{(2n01)}$, $c_{in2}^{(2n)}$, and $c_{in2}^{(2n01)}$ (n 1, 2, $\cdots$) must satisfy

$$c_{in1}^{(2n)}(s, 0^0) \quad c_1^{(2n01)}(s, 0^/) \; / \; c_1^{(2n)}(s, 0^/),$$
$$\text{(on plate 1),} \qquad [3.21]$$

$$e_1\,\frac{í c_{in1}^{(2n)}}{í z}\bigg|_{z\;0^0} \; 0\;e\,\frac{í(c_1^{(2n01)} \; / \; c_1^{(2n)})}{í z}\bigg|_{z\;0^/} \quad 0,$$
$$\text{(on plate 1),} \qquad [3.22]$$

$$c_{in2}^{(2n01)}(a^0, u) \quad c_1^{(2n02)}(a^/, u) \; / \; c_1^{(2n01)}(a^/, u),$$
$$\text{(on sphere 2),} \qquad [3.23]$$

$$e_2\,\frac{í c_{in2}^{(2n01)}}{í r}\bigg|_{r\;a^0} \; 0\;e\,\frac{í(c_1^{(2n02)} \; / \; c_1^{(2n01)}}{í r}\bigg|_{r\;a^/} \quad 0,$$
$$\text{(on sphere 2),} \qquad [3.24]$$

$$c_{in1}^{(2n01)}(s, 0^0) \quad c_2^{(2n02)}(s, 0^/) \; / \; c_2^{(2n01)}(s, 0^/),$$
$$\text{(on plate 1),} \qquad [3.25]$$

$$e_1\,\frac{í c_{in1}^{(2n01)}}{í z}\bigg|_{z\;0^0} \; 0\;e\,\frac{í(c_1^{(2n02)} \; / \; c_1^{(2n01)})}{í z}\bigg|_{z\;0^/} \quad 0,$$
$$\text{(on plate 1),} \qquad [3.26]$$

$$c_{in2}^{(2n)}(a^0, u) \quad c_2^{(2n01)}(a^/, u) \;/\; c_2^{(2n)}(a^/, u),$$

$$\text{(on sphere 2)}, \quad [3.27]$$

$$e_2 \left.\frac{í\, c_{in2}^{(2n)}}{í r}\right|_{r\ a^0} \; 0 \; e \left.\frac{í(c_2^{(2n01)} \;/\; c_2^{(2n)})}{í r}\right|_{r\ a^/} \quad 0.$$

$$\text{(on sphere 2)}, \quad [3.28]$$

so that the boundary conditions [3.4]–[3.7] are satisfied.

The explicit forms for several terms are given below. The term $c_1^{(1)}$ is given by

$$c_1^{(1)}(r, u) \quad c_{01} e^{0\,k(H\,/\,a_2)} \sqrt{\frac{p}{2k}} \sum_{n\ 0}^{\infty} (2n \;/\; 1)$$

$$1 \;\; H_n(2)\, \frac{K_{n\,/\,1/2}(kr)}{\sqrt{r}}\, P_n(\cos u), \quad [3.29]$$

which can be rewritten on the basis of the coordinate system (s, z), viz.,

$$c_1^{(1)}(s, z) \quad c_{01}\, \frac{p}{2k} \exp[\,0\,k(H \;/\; a_2)]$$

$$1 \int_0^{\infty} \frac{\exp[\,0\sqrt{k^2 \;/\; k^2}(H \;/\; a_2\;0\;z)]}{\sqrt{k^2 \;/\; k^2}}$$

$$1 \sum_{n\ 0}^{\infty} (2n \;/\; 1) H_n(2) P_n\!\left(\frac{\sqrt{k^2 \;/\; k^2}}{k}\right) J_0(ks)\, k dk.$$

$$[3.30]$$

The term $c_{in2}^{(1)}$ is

$$c_{in2}^{(1)}(r, u) \quad c_{01} e^{0\,k(H\,/\,a_2)} \sqrt{\frac{p}{2k a_2}} \sum_{n\ 0}^{\infty} (2n \;/\; 1) \left(\frac{r}{a_2}\right)^n$$

$$1 \;\; [I_{n\,/\,1/2}(ka_2) \;/\; H_n(2) K_{n\,/\,1/2}(ka_2)]$$

$$1 \;\; P_n(\cos u), \quad [3.31]$$

where

$$H_n(2) \quad 0\; \frac{I^{\star}_{n\,/\,1/2}(ka_2) \;0\; (1 \;/\; 2n e_2/e) I_{n\,/\,1/2}(ka_2)/2ka_2}{K^{\star}_{n\,/\,1/2}(ka_2) \;0\; (1 \;/\; 2n e_2/e) K_{n\,/\,1/2}(ka_2)/2ka_2}$$

$$\frac{I_{n\,0\,1/2}(ka_2) \;0\; (n \;/\; 1 \;/\; n e_2/e) I_{n\,/\,1/2}(ka_2)/ka_2}{K_{n\,0\,1/2}(ka_2) \;/\; (n \;/\; 1 \;/\; n e_2/e) K_{n\,/\,1/2}(ka_2)/ka_2}.$$

$$[3.32]$$

The term $c_1^{(2)}$ is

$$c_1^{(2)}(s, z) \quad 0\; c_{01}\, \frac{p}{2k}\, e^{0\,k(H\,/\,a_2)} \sum_{n\ 0}^{\infty} (2n \;/\; 1) H_n(2)$$

$$1 \int_0^{\infty} \frac{e_1 k \;0\; e\sqrt{k^2 \;/\; k^2}}{e_1 k \;/\; e\sqrt{k^2 \;/\; k^2}}$$

$$1 \;\; \frac{\exp[\,0\sqrt{k^2 \;/\; k^2}(H \;/\; a_2\;0\;z)]}{\sqrt{k^2 \;/\; k^2}}$$

$$1 \;\; P_n\!\left(\frac{\sqrt{k^2 \;/\; k^2}}{k}\right) J_0(ks)\, k dk, \quad [3.33]$$

which can be rewritten in the (r, u) coordinate system as

$$c_1^{(2)}(r, u) \quad c_{01} \sqrt{\frac{p}{2k}}\, e^{0\,k(H\,/\,a_2)}$$

$$1 \sum_{n\ 0}^{\infty} \sum_{m\ 0}^{\infty} (2n \;/\; 1)(2m \;/\; 1)$$

$$1 \;\; g_{nm} H_n(2)\, \frac{I_{m\,/\,1/2}(kr)}{\sqrt{r}}\, P_n(\cos u), \quad [3.34]$$

where

$$g_{nm} \quad 0\; \frac{p}{2k} \int_0^{\infty} \frac{e_1 k \;0\; e\sqrt{k^2 \;/\; k^2}}{e_1 k \;/\; e\sqrt{k^2 \;/\; k^2}}$$

$$1 \;\; \frac{\exp[\,0\,2\sqrt{k^2 \;/\; k^2}(H \;/\; a_2)]}{\sqrt{k^2 \;/\; k^2}}$$

$$1 \;\; P_n\!\left(\frac{\sqrt{k^2 \;/\; k^2}}{k}\right) P_m\!\left(\frac{\sqrt{k^2 \;/\; k^2}}{k}\right) k dk$$

$$\frac{p}{2} \int_1^{\infty} \frac{et \;0\; e_1\sqrt{t^2 \;0\; 1}}{et \;/\; e_1\sqrt{t^2 \;0\; 1}}\, e^{0\,2kt(H\,/\,a_2)} P_n(t) P_m(t)\, dt. \quad [3.35]$$

For the special case where n 0 or m 0,

$$g_{n0} \quad g_{0n} \quad \sqrt{\frac{p}{4k(H \;/\; a_2)}}\, K_{n\,/\,1/2}(2k(H \;/\; a_2))$$

$$0\; \frac{p}{k} \int_0^{\infty} \frac{e_1 \exp[\,0\,2\sqrt{k^2 \;/\; k^2}(H \;/\; a_2)]}{(e_1 k \;/\; e\sqrt{k^2 \;/\; k^2})\sqrt{k^2 \;/\; k^2}}$$

$$1 \;\; P_n\!\left(\frac{\sqrt{k^2 \;/\; k^2}}{k}\right) k^2 dk, \quad [3.36]$$

and for n m 0,

$$g_{00} \quad \frac{p e^{0\,2k(H\,/\,a_2)}}{4k(H \;/\; a_2)} \;0\; \frac{p}{k} \int_0^{\infty}$$

$$1 \;\; \frac{e_1 \exp[\,0\,2\sqrt{k^2 \;/\; k^2}(H \;/\; a_2)]}{(e_1 k \;/\; e\sqrt{k^2 \;/\; k^2})\sqrt{k^2 \;/\; k^2}}\, k^2 dk. \quad [3.37]$$

The free energy $F(H)$ of the present system at low potentials is given by (1):

$$
\begin{aligned}
F(H) \quad & / \tfrac{1}{2} \int_{S_1} \mathrm{s}_1 \mathrm{c}_{01} dS_1 \; / \; \tfrac{1}{2} \int_{S_2} \mathrm{s}_2 \mathrm{c}_{01} dS_2 \\
& / \tfrac{1}{2} \mathrm{s}_1 \int_0^{\infty} \mathrm{c}_2(s,\, 0) 2\mathrm{p} s ds \\
& / \; \tfrac{1}{2} \mathrm{s}_2 \int_0^{\mathrm{p}} \mathrm{c}_2(a_2,\, \mathrm{u}) 2\mathrm{p} a_2^2 \sin \mathrm{u} d\mathrm{u}. \qquad [3.38]
\end{aligned}
$$

Substituting the obtained expressions for c into Eq. [3.38], we obtain the required result for the interaction energy between plate 1 and spheres 1 and 2 at constant surface charge density, viz.,

$$
\begin{aligned}
V(H) \quad & 4\mathrm{pee}_0 \mathrm{c}_{01} \mathrm{c}_{02} a_2 e^{0\,\mathrm{k}H} \; / \; \mathrm{p}^2 \mathrm{ee}_0 \mathrm{c}_{01}^2 \frac{1}{\mathrm{k}} e^{0\,2\mathrm{k}(H/a_2)} \\
& 1 \sum_{n \; 0}^{\infty} (2n \; / \; 1) H_n(2) \; / \; 4\mathrm{ee}_0 \mathrm{c}_{02}^2 \mathrm{k} a_2^2 e^{2\mathrm{k} a_2} \mathrm{g}_{00} \\
& / \; 2\mathrm{pee}_0 \mathrm{c}_{01} \mathrm{c}_{02} a_2 e^{0\,\mathrm{k}H} \sum_{n \; 0}^{\infty} (2n \; / \; 1)(\mathrm{g}_{0n} \; / \; \mathrm{g}_{n0}) \\
& 1 \; H_n(2) \; / \; \mathrm{p}^2 \mathrm{ee}_0 \mathrm{c}_{01}^2 \frac{1}{\mathrm{k}} \mathrm{c}_{02} e^{0\,2\mathrm{k}(H/a_2)} \sum_{n \; 0}^{\infty} \sum_{m \; 0}^{\infty} \\
& 1 \; (2n \; / \; 1)(2m \; / \; 1) \mathrm{g}_{nm} H_n(2) H_m(2) \\
& / \; 4\mathrm{ee}_0 \mathrm{c}_{02}^2 \mathrm{k} a_2^2 e^{2\mathrm{k} a_2} \sum_{n \; 0}^{\infty} (2n \; / \; 1) \mathrm{g}_{0n} \mathrm{g}_{n0} H_n(2) \\
& / \; 2\mathrm{pee}_0 \mathrm{c}_{01} \mathrm{c}_{02} a_2 e^{0\,\mathrm{k}H} \sum_{n \; 0}^{\infty} \sum_{m \; 0}^{\infty} (2n \; / \; 1)(2m \; / \; 1) \\
& 1 \; \mathrm{g}_{nm}(\mathrm{g}_{0n} \; / \; \mathrm{g}_{m0}) H_n(2) H_m(2) \; / \; \cdots \\
& / \; 2\mathrm{pee}_0 \mathrm{c}_{01} \mathrm{c}_{02} a_2 e^{0\,\mathrm{k}H} \sum_{n_1 \; 0}^{\infty} \sum_{n_2 \; 0}^{\infty} \cdots \sum_{n_\mathrm{n} \; 0}^{\infty} \\
& 1 \; (2n_1 \; / \; 1)(2n_2 \; / \; 1) \cdots (2n_\mathrm{n} \; / \; 1) \\
& 1 \; \mathrm{g}_{n_1 n_2} \mathrm{g}_{n_2 n_3} \cdots \mathrm{g}_{n_{\mathrm{n}\,0\,1} n_\mathrm{n}} (\mathrm{g}_{0 n_1} \; / \; \mathrm{g}_{n_\mathrm{n} 0}) H_{n_1}(2) \\
& 1 \; H_{n_2}(2) \cdots H_{n_\mathrm{n}}(2) \; / \; \mathrm{p}^2 \mathrm{ee}_0 \mathrm{c}_{01}^2 \frac{1}{\mathrm{k}} e^{0\,2\mathrm{k}(H/a_2)} \\
& 1 \sum_{n_1 \; 0}^{\infty} \sum_{n_2 \; 0}^{\infty} \cdots \sum_{n_\mathrm{n} \; 0}^{\infty} \\
& 1 \; (2n_1 \; / \; 1)(2n_2 \; / \; 1) \cdots (2n_\mathrm{n} \; / \; 1) \\
& 1 \; \mathrm{g}_{n_1 n_2} \mathrm{g}_{n_2 n_3} \cdots \mathrm{g}_{n_{\mathrm{n}\,0\,1} n_\mathrm{n}} H_{n_1}(2) H_{n_2}(2) \cdots H_{n_\mathrm{n}}(2) \\
& / \; 4\mathrm{ee}_0 \mathrm{c}_{02}^2 \mathrm{k} a_2^2 e^{2\mathrm{k} a_2} \sum_{n_1 \; 0}^{\infty} \sum_{n_2 \; 0}^{\infty} \cdots \sum_{n_\mathrm{n} \; 0}^{\infty} \\
& 1 \; (2n_1 \; / \; 1)(2n_2 \; / \; 1) \cdots (2n_\mathrm{n} \; / \; 1) \\
& 1 \; \mathrm{g}_{n_1 n_2} \mathrm{g}_{n_2 n_3} \cdots \mathrm{g}_{n_{\mathrm{n}\,0\,1} n_\mathrm{n}} \mathrm{g}_{0 n_1} \mathrm{g}_{n_\mathrm{n} 0} H_{n_1}(2) \\
& 1 \; H_{n_2}(2) \cdots H_{n_\mathrm{n}}(2) \; / \; \cdots \qquad [3.39]
\end{aligned}
$$

Note that Eq. [3.39] is obtained by replacing $G_n(2)$ and b_{nm} in Eq. [2.39] by $H_n(2)$ and $0\ \mathrm{g}_{nm}$, respectively.

4. MIXED CASE

An expression for the interaction energy for the mixed cases where either of plate 1 or sphere 2 has a constant surface potential and the other has a constant surface charge density can also be obtained. It can easily be shown that when plate 1 has a constant surface potential and sphere 2 has a constant surface charge density, the interaction energy is given by Eq. [2.39] with $G_n(2)$ replaced by $H_n(2)$. When plate 1 has a constant surface charge density and sphere 2 has constant surface potential, the interaction energy is given by Eq. [2.39] with b_{nm} replaced by $0\ \mathrm{g}_{nm}$.

5. RESULTS AND DISCUSSION

We have derived explicit exact analytic expressions for the interaction energy between a platelike particle and a spherical particle on the basis of the linearized Poisson–Boltzmann equation. Both particles are rigid and ion-impenetrable. When the surface potentials of the interacting particles remain constant, the interaction energy is given by Eq. [2.39]. If, on the other hand, the surface charge densities of the interacting particles remain constant, then the interaction energy is given by Eq. [3.39]. The interaction energy expressions are also derived for the mixed case in which one particle has a constant surface potential and the other constant surface charge density. We have confirmed numerically that the results obtained in the present paper agree with the previous results when the radius of either one sphere tends to infinity (6, 7, 9, 10).

The first term in each of Eqs. [2.39] and [3.39] corresponds to the interaction energy obtained by the linear superposition approximation. If plate 1 and sphere 2 were both ion-penetrable (or soft particles), the interaction energy would be given by only this term (3). If plate 1 is soft and sphere 2 is hard with constant surface potential (or constant surface charge density), then the interaction energy is given by the first term plus the second term in Eq. [2.39] (or in Eq. [3.39]). If plate 1 is hard with constant surface potential (or constant surface charge density) and sphere 2 is soft, then the interaction energy is given by the first term plus the third term in Eq. [2.39] (or in Eq. [3.39]) (4, 8). The second term in each of Eqs. [2.39] and [3.39], which depends only on the unperturbed surface potential c_{01} of plate 1 and does not depend on the unperturbed surface potential c_{02} of sphere 2, corresponds to the image interaction between plate 1 and its image with respect to sphere 2. The third term in each of Eqs. [2.39] and [3.39], on the other hand, corresponds to the image interaction between sphere 2 and its image with respect to plate 1. If plate 1 and sphere 2 are both hard, the interaction energy is given in terms of infinite series, as in Eqs. [2.39] and [3.39].

As Chan and Chan (27) pointed out, the force between a plate whose surface potential is always zero and a sphere at separation H is identical with the force between two spheres at separation $2H$ having unperturbed surface potentials of same magnitude but opposite sign (i.e., $\psi_{01}^{(0)} = -\psi_{02}^{(0)}$) and the interaction energy for the former case is half that for the latter case. Also the force between a plate whose surface charge density is always zero (and permittivity is zero) and a sphere at separation H is identical with the force between two identical spheres (i.e., $\psi_{01}^{(0)} = \psi_{02}^{(0)}$) at separation $2H$ and the interaction energy for the former case is half that for the latter case. We have confirmed that these relations hold analytically for the obtained energy expressions.

Consider the case where $\kappa a_2 \gg 1$ (see Appendix). For the constant surface potential case, Eq. [2.39] becomes

$$V(H) = 4\pi\varepsilon\varepsilon_0 a_2\left[\psi_{01}\psi_{02}e^{-\kappa H} - \tfrac{1}{4}\left(\psi_{01}^2 + \psi_{02}^2\frac{a_2}{a_2+H}\right)e^{-2\kappa H}\right] + O(e^{-3\kappa H}). \qquad [5.1]$$

For the constant surface charge density case, if ε_1 and ε_2 are finite, Eq. [3.39] becomes

$$V(H) = 4\pi\varepsilon\varepsilon_0 a_2\left[\psi_{01}\psi_{02}e^{-\kappa H} + \tfrac{1}{4}\psi_{01}^2 e^{-2\kappa H} \times \left\{1 - \frac{\varepsilon_2}{\varepsilon}\sqrt{\frac{\pi}{\kappa a_2}}\right\} + \tfrac{1}{4}\psi_{02}^2 e^{-2\kappa H}\frac{a_2}{a_2+H} \times \left\{1 - \frac{\varepsilon_1}{\varepsilon}\sqrt{\frac{\pi}{\kappa(H+a_2)}}\right\}\right] + O(e^{-3\kappa H}),$$

$$\left(\frac{\varepsilon_1}{\varepsilon}\sqrt{\frac{\pi}{\kappa(H+a_2)}} \ll 1,\ \frac{\varepsilon_2}{\varepsilon}\sqrt{\frac{\pi}{\kappa a_2}} \ll 1\right), \qquad [5.2]$$

and if ε_1 and ε_2 are infinity (plate 1 and sphere 2 are both metallic),

$$V(H) = 4\pi\varepsilon\varepsilon_0 a_2\left[\psi_{01}\psi_{02}e^{-\kappa H} - \tfrac{1}{4}\left(\psi_{01}^2 + \psi_{02}^2\frac{a_2}{a_2+H}\right)e^{-2\kappa H}\right] + O(e^{-3\kappa H}),$$

$$(\varepsilon_1 = \infty \text{ and } \varepsilon_2 = \infty). \qquad [5.3]$$

For the mixed case where plate 1 has a constant surface potential and sphere 2 has a constant surface charge density with finite ε_2,

$$V(H) = 4\pi\varepsilon\varepsilon_0 a_2\left[\psi_{01}\psi_{02}e^{-\kappa H} + \tfrac{1}{4}\psi_{01}^2 e^{-2\kappa H}\left(1 - \frac{\varepsilon_2}{\varepsilon}\sqrt{\frac{\pi}{\kappa a_2}}\right) - \tfrac{1}{4}\psi_{02}^2 e^{-2\kappa H}\frac{a_2}{a_2+H}\right] + O(e^{-3\kappa H}),$$

$$\left(\frac{\varepsilon_2}{\varepsilon}\sqrt{\frac{\pi}{\kappa a_2}} \ll 1\right). \qquad [5.4]$$

When plate 1 has a constant surface potential and sphere 2 has a constant surface charge density with infinite ε_2 (sphere 2 is metallic),

$$V(H) = 4\pi\varepsilon\varepsilon_0 a_2\left[\psi_{01}\psi_{02}e^{-\kappa H} - \tfrac{1}{4}\psi_{01}^2 e^{-2\kappa H} - \tfrac{1}{4}\psi_{02}^2 e^{-2\kappa H}\frac{a_2}{a_2+H}\right] + O(e^{-3\kappa H}),$$

$$(\varepsilon_2 = \infty). \qquad [5.5]$$

When plate 1 has a constant surface charge density with finite ε_1 and sphere 2 has a constant surface potential,

$$V(H) = 4\pi\varepsilon\varepsilon_0 a_2\left[\psi_{01}\psi_{02}e^{-\kappa H} - \tfrac{1}{4}\psi_{01}^2 e^{-2\kappa H} + \tfrac{1}{4}\psi_{02}^2 e^{-2\kappa H}\frac{a_2}{a_2+H}\left\{1 - \frac{\varepsilon_1}{\varepsilon}\sqrt{\frac{\pi}{\kappa(H+a_2)}}\right\}\right] + O(e^{-3\kappa H}),\ \left(\frac{\varepsilon_1}{\varepsilon}\sqrt{\frac{\pi}{\kappa(H+a_2)}} \ll 1\right). \qquad [5.6]$$

When plate 1 has a constant surface charge density with infinite ε_1 and sphere 2 has a constant surface potential,

$$V(H) = 4\pi\varepsilon\varepsilon_0 a_2[\psi_{01}\psi_{02}e^{-\kappa H} - \tfrac{1}{4}(\psi_{01}^2 + \psi_{02}^2)e^{-2\kappa H}] + O(e^{-3\kappa H}),\ (\varepsilon_1 = \infty). \qquad [5.7]$$

These results agree with the results derived by applying Derjaguin's approximation (12), for the constant surface potential case (13), the constant surface charge density case (with $\varepsilon_1 = \varepsilon_2 = 0$) (14), and the mixed case (with zero particle permittivity) (15).

Finally we compare the image interactions appearing in the present theory with the usual image interaction. For this purpose we consider the case where the surface charge density of plate 1 is always zero ($\psi_{01} = 0$) and $\kappa a \to 0$, since the usual image interaction refers to a point charge interacting with a uncharged plate. In the case of c_{01} 0, the interaction energy (Eq. [3.39]) becomes

$$
\begin{aligned}
V(H) \quad & 4ee_0 c_{02}^2 ka_2^2 e^{2ka_2} g_{00} \;/\; 4ee_0 c_{02}^2 ka_2^2 e^{2ka_2} \\
& 1 \sum_{n\;0}^{\infty} (2n \;/\; 1) g_{0n} g_{n0} H_n(2) \;/\; \cdots \\
& /\; 4ee_0 c_{02}^2 ka_2^2 e^{2ka_2} \sum_{n_1\;0}^{\infty} \sum_{n_2\;0}^{\infty} \cdots \\
& 1 \sum_{n_n\;0}^{\infty} (2n_1 \;/\; 1)(2n_2 \;/\; 1)\cdots(2n_n \;/\; 1) \\
& 1 \; g_{n_1 n_2} g_{n_2 n_3} \cdots g_{n_{n\,0\,1} n_n} g_{0 n_1} g_{n_n 0} \\
& 1 \; H_{n_1}(2) H_{n_2}(2) \cdots H_{n_n}(2) \;/\; \cdots \qquad [5.8]
\end{aligned}
$$

In the limit $ka \to 0$, all the terms on the right hand side except the first term vanish and g_{00} tends to

$$g_{00} \to \frac{p}{4kH} \frac{e \; 0 \; e_1}{e \;/\; e_1}. \qquad [5.9]$$

We introduce the total charge Q $4pa^2 s$ on sphere 2, which is related to the unperturbed surface potential c_{02} of sphere 2 by

$$c_{02} \quad \frac{Q}{4pee_0 a_2 (1 \;/\; ka_2)}. \qquad [5.10]$$

Equation [5.8] then tends to

$$V(H) \quad \frac{Q^2 e^{0\,kH}}{16pee_0 H} \frac{e \; 0 \; e_1}{e \;/\; e_1}. \qquad [5.11]$$

This is the screened image interaction between a point charge and an uncharged plate, both immersed in an electrolyte solution of Debye–Hückel parameter k. Further, in the absence of electrolytes ($k \to 0$), Eq. [5.11] becomes

$$V(H) \quad \frac{Q^2}{16pee_0 H} \frac{e \; 0 \; e_1}{e \;/\; e_1}, \qquad [5.12]$$

which is the usual image interaction energy (28).

Figure 4 illustrates how the image interaction between a spherical particle of finite size and a plate calculated from Eq. [5.8] approaches the usual image interaction between a point charge and a plate for the two cases e_1 0 and e_1 ∞ (Eq. [5.11]). In the former case the interaction force is repulsion and the latter case attraction. We can thus conclude that Eq. [5.8] is a generalization of the usual image interaction of point charge to a colloidal particle of finite size.

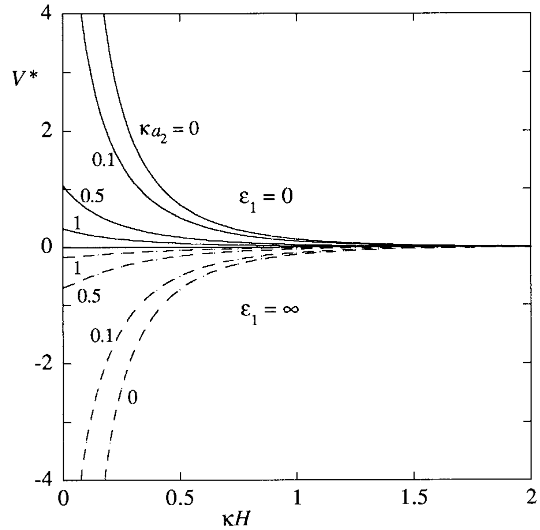

FIG. 4. Reduced potential energy V^* $16pee_0 V/kQ^2$ of the image interaction between a hard sphere (sphere 2) of radius a_2 with e_2 0 and a hard plate (plate 1) as a function of kH for several values of the reduced radius ka_2 of sphere 2. Calculated with Eq. [5.8]. Solid lines, e_1 0; dashed lines, e_1 ∞ (plate 1 is a metal).

APPENDIX

We give below several approximate relations applicable for large ka_2. For large x, $I_{n\,/\,1/2}$ and $K_{n\,/\,1/2}$ are approximated as follows (29).

$$I_{n\,/\,1/2}(x) \quad \frac{e^x}{\sqrt{2px}} \left(1 \; 0 \; \frac{1}{x}\right)^m, \qquad [A1]$$

$$K_{n\,/\,1/2}(x) \quad \sqrt{\frac{p}{2x}} \, e^{0x} \left(1 \;/\; \frac{1}{x}\right)^m, \qquad [A2]$$

with

$$m \quad \frac{(n \;/\; \frac{1}{2})^2}{2} \; 0 \; \tfrac{1}{8}. \qquad [A3]$$

On the basis of the above approximate forms for $I_{n\,/\,1/2}$ and $K_{n\,/\,1/2}$, the sum appearing in Eq. [2.39] can be approximated in the following way.

$$
\begin{aligned}
& e^{0\,2ka_2} \sum_{n\;0}^{\infty} (2n \;/\; 1) G_n(2) \quad 0\, e^{0\,2ka_2} \sum_{n\;0}^{\infty} (2n \;/\; 1) \\
& 1 \; \frac{I_{n\,/\,1/2}(ka_2)}{K_{n\,/\,1/2}(ka_2)} \quad 0 \; \frac{1}{p} \sum_{n\;0}^{\infty} (2n \;/\; 1) \\
& 1 \left(\frac{1 \; 0 \; (1/ka_2)}{1 \;/\; (1/ka_2)} \right)^{1/2(n\,/\,(1/2))^2 0\,(1/8)} \\
& 0 \; \frac{2}{p} \int_0^{\infty} x \left(1 \; 0 \; \frac{2}{ka_2}\right)^{x^2/2\,0\,(1/8)} dx \quad 0 \; \frac{ka_2}{p}. \qquad [A4]
\end{aligned}
$$

Similarly the sum in Eq. [3.39] can be approximated as

$$e^{\,0\,2\mathrm{k}a_2}\sum_{n\ \ 0}^{\infty}(2n\ \ /\ \ 1)H_n(2)$$

$$\begin{cases} \dfrac{\mathrm{k}a_2}{\mathrm{p}}\left(1\ \ 0\ \dfrac{\mathrm{e}_2}{\mathrm{e}}\sqrt{\dfrac{\mathrm{p}}{\mathrm{k}a_2}}\right),\ \left(\dfrac{\mathrm{e}_2}{\mathrm{e}}\sqrt{\dfrac{\mathrm{p}}{\mathrm{k}a_2}} \ll 1\right). \\ 0\ \dfrac{\mathrm{k}a_2}{\mathrm{p}},\ (\mathrm{e}_2\quad \infty). \end{cases} \qquad [A5]$$

Also, g_{00} can be approximated as

$$\mathrm{g}_{00}\quad \begin{cases} \dfrac{\mathrm{p}\ \exp[\,0\,2\mathrm{k}(H\ \ /\ \ a_2)]}{4\mathrm{k}(H\ \ /\ \ a_2)}\left\{1\ \ 0\ \dfrac{\mathrm{e}_1}{\mathrm{e}}\sqrt{\dfrac{\mathrm{p}}{\mathrm{k}(H\ \ /\ \ a_2)}}\right\}, \\ \qquad\qquad \left(\dfrac{\mathrm{e}_1}{\mathrm{e}}\sqrt{\dfrac{\mathrm{p}}{\mathrm{k}(H\ \ /\ \ a_2)}} \ll 1\right), \\ 0\ \dfrac{\mathrm{p}\ \exp[\,0\,2\mathrm{k}(H\ \ /\ \ a_2)]}{4\mathrm{k}(H\ \ /\ \ a_2)},\ (\mathrm{e}_1\quad \infty), \end{cases} \qquad [A6]$$

where the integral in Eq. [3.37] can be obtained easily for the special cases of $\mathrm{e}_1\quad 0$ and $\mathrm{e}_1\quad \infty$. An approximate form for finite values of e_1 is given in Eq. [52] of Ref. (8).

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