Journal of Colloid and Interface Science **218,** 423–432 (1999)
Article ID jcis.1999.6417, available online at http://www.idealibrary.com on IDEAL®

Electrical Double-Layer Interaction between Charged Particles near Surfaces and in Confined Geometries

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Received December 31, 1998; accepted July 12, 1999

The proximity effect of one or two flat surfaces on the double-layer interaction between two identically charged colloidal particles immersed in an electrolyte is examined. Simple analytical formulas are presented for the interaction of (i) two particles in the vicinity of a charged flat surface and (ii) two particles confined between two parallel plates. It is found that the surface(s) can strongly influence the pairwise interaction of the particles, leading to increase, decrease, or even elimination of the electrostatic interaction, in comparison to the corresponding result in an unbounded electrolyte. © 1999 Academic Press

Key Words: **confined geometries; electrostatic interactions; Poisson–Boltzmann.**

1. INTRODUCTION

The electrical double-layer interaction between two charged spheres immersed in an unbounded electrolyte has been studied extensively over the past 50 years, during which time the validity and accuracy of the well-known Poisson–Boltzmann theory has been rigorously examined and established (1). Despite the extensive amount of work reported on this problem, surprisingly very little is known theoretically about the effects of geometrical confinement on the pairwise double-layer interaction between two particles. Experimental results suggest, however, that geometrical confinement can have a dramatic effect on this pairwise interaction (2–6). In particular, an attractive interaction between identical particles at low electrolyte concentrations has been reported when the particles are in the vicinity of a charged surface or confined between two charged plates (2–6). This observation has defied many attempts at theoretical explanation (7–11) and still remains an open problem (12). Furthermore, it has been proven that the Poisson–Boltzmann theory always gives a repulsive interaction, irrespective of whether the particles are confined or unconfined (12, 13). It remains to be seen whether the source of this dichotomy lies in the interpretation of experimental results or in features not captured in the existing and established theories. Such questions, however, lie outside the scope of the present paper. Instead we shall implement the established Poisson–Boltzmann theory and examine the effects of geometrical confinement on the electrical double-layer interaction between two charged spheres. We shall restrict our discussion to the low-potential limit and thus use the linearized Poisson–Boltzmann theory, although the features and properties of the interaction found in this limit are certainly expected to be found for higher potentials as well.

Previous work on this problem was also performed within the framework of the linearized Poisson–Boltzmann theory (14, 15). Chang *et al.* (14) examined the effects of confining two colloidal particles between two parallel glass plates and found that the glass plates increased the magnitude of the repulsive interaction. Medina-Noyola *et al.* (15) extended the work of Chang *et al.* (14) to consider some modified configurations, including particles at a dielectric–electrolyte interface and particles confined between two dielectric plates, where the position of the particles is not necessarily at the median-plane between the plates. However, in both these analyses the particles were treated as point charges and the confining surfaces were assumed to have the properties of a dielectric discontinuity. The true electrical properties of the particles and surfaces were not taken into account, which restricted the applicability of their results. In contrast, we examine the pairwise interaction between two spherical particles of finite size and specified electrical properties that are (i) in the vicinity of a single charged flat plate or (ii) confined between two charged parallel plates. The particles and the plate(s) are taken to be of either the constant charge or the constant potential type, and consequently finite size effects of the particles are included in the analysis. We note that any other surface charge properties, such as charge regulation due to the dissociation of surface groups (16), must lie within the limiting cases of constant potential and constant charge (16). We find that the pairwise interaction can be influenced significantly by the presence of the confining surface(s), and is strongly dependent on the electrical properties of the particles and the surface(s).

2. THEORETICAL FORMULATION

2a. Particles Near a Single Plate

We begin by considering two identical spherical particles immersed in an electrolyte, in the presence of a single flat plate. It is assumed that the spherical particles have a center-to-center separation R, are at the same sphere-center to plate distance

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0021-9797/99 $30.00

$(H/2)$, and have identical radii a and electrical properties. In particular, the spherical particles have either uniform constant surface charge densities (CC) or uniform constant surface potentials (CP). The flat plate also has the property of either CC or CP, but this need not be identical to the properties of the spheres. For the case of a CC plate or a CC sphere, we assume that the dielectric constant or relative permittivity of the plate or sphere is zero. This is a reasonable approximation for the case of aqueous electrolytes (16). To calculate the interaction free energy, the electrical potential ψ in the electrolyte is required. Within the framework of the linearized Poisson–Boltzmann theory, ψ satisfies

$$\nabla^2\psi - \kappa^2\psi = 0, \qquad [1]$$

where κ is the Debye screening parameter of the electrolyte.

It is expected that the pairwise sphere–sphere interaction can be strongly affected by the presence of the flat plate only if $\kappa H < O(1)$ and $\kappa a < O(1)$. Therefore, it is appropriate in the first instance to consider the limiting case of $\kappa a \to 0$, corresponding to two point charges, which will then be used to construct the solution for finite κa. For $\kappa a \to 0$, the exact analytical solution to the electrical potential ψ may be easily obtained using the method of images (17). We note that the sign of the image charges will depend on the electrical properties of the plate. For a CP plate the image charges will be opposite in sign to that of the source charges, whereas for a CC plate the images charges will have the same sign. The interaction free energy $\Delta F(R)$ required to bring the charges from an infinite separation $R \to \infty$ to a finite separation R, at fixed sphere–plate separation $(H/2)$, may then be calculated by taking the sum of the individual source–source and source–image contributions. Following this procedure, we obtain the limiting solution as $\kappa a \to 0$,

$$\Delta F(R) = \frac{Q^2}{4\pi\epsilon}\left(\frac{e^{-\kappa R}}{R} \pm \frac{e^{-\kappa\sqrt{R^2+H^2}}}{\sqrt{R^2+H^2}}\right), \qquad [2]$$

where the upper and lower sign in $\pm$ corresponds to a CC and a CP plate, respectively, Q is the charge of the spheres, and ϵ is the permittivity of the electrolyte.

Equation [2] may now be modified to take into account the finite size effects of the spheres and incorporate their corresponding electrical properties. At this stage we note that [2] is a monopole–monopole result. Therefore, to account for the finite size effects of the spheres, we only consider the surface averaged conditions on each sphere. In particular, for a CP sphere we ensure that the average surface potential is set to the true surface potential, whereas for a CC sphere, we set the average surface charge density to the actual surface charge density. To be consistent with the well-known unconfined superposition result (18), this calculation is performed by taking each sphere in isolation from the other sphere. Following the above methodology, we then obtain the final result for the interaction free energy

$$\Delta F(R) = 4\pi\epsilon a^2 \Phi_{\mathrm{eff}}^2 e^{2\kappa a} g_1(R), \qquad [3]$$

where

$$g_1(R) = \frac{e^{-\kappa R}}{R} \pm \frac{e^{-\kappa\sqrt{R^2+H^2}}}{\sqrt{R^2+H^2}}, \qquad [4a]$$

$$\Phi_{\mathrm{eff}} = \frac{\Phi_{\mathrm{s}}^{\mathrm{iso}} - \Phi_{\mathrm{p}}^{\mathrm{iso}}\Gamma e^{-\kappa H/2}}{1 \pm \dfrac{a}{H}\Gamma e^{-\kappa(H-a)}}, \qquad [4b]$$

$$\Gamma = \begin{cases} \dfrac{\sinh \kappa a}{\kappa a} & : \ CP \text{ spheres} \\ \dfrac{\sinh \kappa a - \kappa a \cosh \kappa a}{\kappa a(1+\kappa a)} & : \ CC \text{ spheres} \end{cases}, \qquad [4c]$$

where $\Phi_{\mathrm{s}}^{\mathrm{iso}}$ and $\Phi_{\mathrm{p}}^{\mathrm{iso}}$ are the surface potentials of the spheres and plate in isolation, respectively, and the upper sign in $\pm$ corresponds to a CC plate whereas the lower sign corresponds to a CP plate.

2b. *Particles Confined between Two Plates*

We now extend the above analysis to the interaction of two identical spherical particles that are confined at the median-plane between two identical and parallel flat plates which are separated a distance H, so that the centers of the spheres are at a distance $(H/2)$ from each plate. All assumptions regarding the properties of the spheres and plates are identical to those discussed above. The analysis then proceeds in an analogous manner to that given above. In particular, the solution for the point charge case $\kappa a \to 0$ is first sought. This is also obtained using the method of images. However, in contrast to the single plate case, we require an infinite number of images to account for the boundary conditions on the plates. The exact result for the interaction free energy in this limiting case $\kappa a \to 0$ directly follows by considering the source–source and all source–image contributions. This result may then be corrected approximately to account for finite size effects, as discussed above, leading to the final expression for the interaction free energy

$$\Delta F(R) = 4\pi\epsilon a^2 \Phi_{\mathrm{eff}}^2 e^{2\kappa a} g_2(R), \qquad [5]$$

where

$$g_2(R) = \frac{e^{-\kappa R}}{R} + 2\sum_{n=1}^{\infty} (\pm 1)^n \frac{e^{-\kappa\sqrt{R^2+H^2n^2}}}{\sqrt{R^2+H^2n^2}}, \qquad [6a]$$

$$\Phi_{\mathrm{eff}} = \frac{\Phi_{\mathrm{s}}^{\mathrm{iso}} - 2\Phi_{\mathrm{p}}^{\mathrm{iso}}\Gamma e^{-\kappa H/2}(1 \mp e^{-\kappa H})^{-1}}{1 - 2\dfrac{a}{H}\Gamma e^{\kappa a}\ln(1 \mp e^{-\kappa H})}, \qquad [6b]$$

where the upper and lower signs in $\pm$ and $\mp$ correspond to CC and CP plates, respectively, whereas all other symbols are as defined above. It will be of value in the discussion below to transform [6a] into the equivalent and exact infinite series

$$g_2(R) = \begin{cases} \dfrac{2}{H}\left(K_0(\kappa R) + 2\sum_{n=1}^{\infty} K_0\left(\kappa R\sqrt{1 + (2\pi n/[\kappa H])^2}\right)\right) & : \quad CC \text{ plates,} \\ \dfrac{4}{H}\sum_{n=0}^{\infty} K_0\left(\kappa R\sqrt{1 + (\pi/[\kappa H])^2(1 + 4n[1 + n])}\right) & : \quad CP \text{ plates} \end{cases} \qquad [7]$$

where $K_0(x)$ is the modified Bessel function of the third kind (19). This transformation is performed by taking the inverse Laplace transform of [6a] and using the properties of elliptic theta functions (19).

3. RESULTS AND DISCUSSION

The formulas presented above are to be compared against the corresponding superposition result for two unconfined identical spherical particles (18)

$$\Delta F(R) = 4\pi\epsilon a^2(\Phi_s^{\text{iso}})^2 e^{2\kappa a}\frac{e^{-\kappa R}}{R}. \qquad [8]$$

Note that [3] and [5] both reduce to the unconfined superposition result [8] in the limit as $\kappa H \to \infty$, as required, and also possess the correct limiting forms for $\kappa a \ll 1$ and $\kappa a \gg 1$, namely, the point charge and unconfined superposition solutions, respectively.

We now examine the implications of the new results. It is evident from [3] and [5] that the interaction is modified in two ways, (i) through the *effective potential* Φ_{eff} and (ii) through the *separation dependencies* $g_1(R)$, $g_2(R)$. In the following sections, we will discuss the behavior of both properties individually, and examine their combined effects.

3a. Effective Potential

From [4b] and [6b] it is clear that the effective potential Φ_{eff} of the spheres is dependent not only on the sphere electrical properties but also on the plate properties and the normalized sphere–plate separation $(\kappa H/2)$. Note that Φ_{eff} is independent of the sphere–sphere separation R. These dependencies can result in either an increase or a decrease in the effective potential Φ_{eff} from its unconfined value Φ_s^{iso}. Furthermore, from [4b] and [6b] it is clear that the effective potential can vanish under certain conditions resulting in zero interaction between the spheres, irrespective of the separation R; i.e., $\Delta F(R) = 0$. For the single-plate case, Eq. [4b], this occurs when the normalized sphere–plate separation $(\kappa H/2)$ is

$$\frac{\kappa H}{2} = \ln(\Gamma\Phi_p^{\text{iso}}/\Phi_s^{\text{iso}}), \qquad [9]$$

irrespective of the boundary conditions on the plate. For particles confined between two plates of the constant charge (CC)

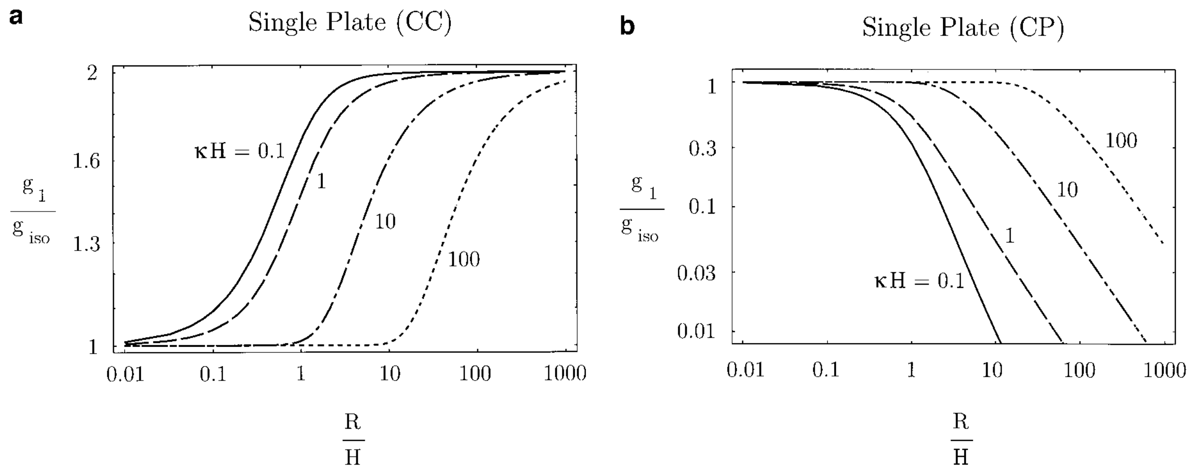

FIG. 1. Plot of ratio $g_1(R)/g_{\text{iso}}(R)$, where $g_{\text{iso}}(R) = e^{-\kappa R}/R$ is the separation dependence for two unconfined spheres. Results shown for a single plate of (a) CC and (b) CP type, for various normalized sphere–plate separations κH and normalized sphere–sphere separations R/H.

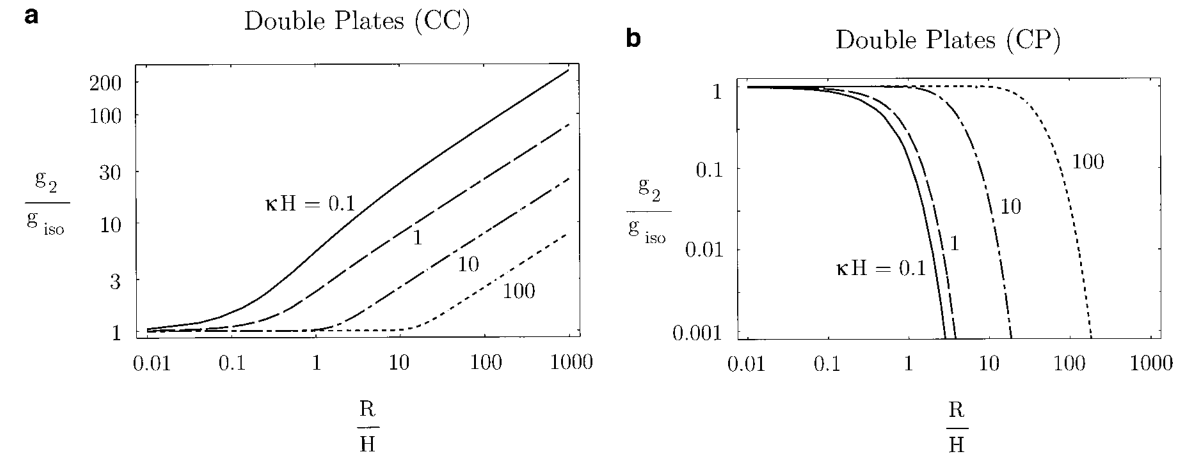

FIG. 2. Plot of ratio $g_2(R)/g_{\mathrm{iso}}(R)$, where $g_{\mathrm{iso}}(R) = e^{-\kappa R}/R$ is the separation dependence for two unconfined spheres. Results shown for double plates of (a) CC and (b) CP type, for various normalized sphere–plate separations κH and normalized sphere–sphere separations R/H.

type, the critical normalized plate spacing κH for which the sphere–sphere interaction free energy ΔF is zero is

$$\kappa H = 2 \sinh^{-1}(\Gamma \Phi_{\mathrm{p}}^{\mathrm{iso}}/\Phi_{\mathrm{s}}^{\mathrm{iso}}), \qquad [10a]$$

whereas for the case when the plates are held at constant potential (CP),

$$\kappa H = 2 \cosh^{-1}(\Gamma \Phi_{\mathrm{p}}^{\mathrm{iso}}/\Phi_{\mathrm{s}}^{\mathrm{iso}}). \qquad [10b]$$

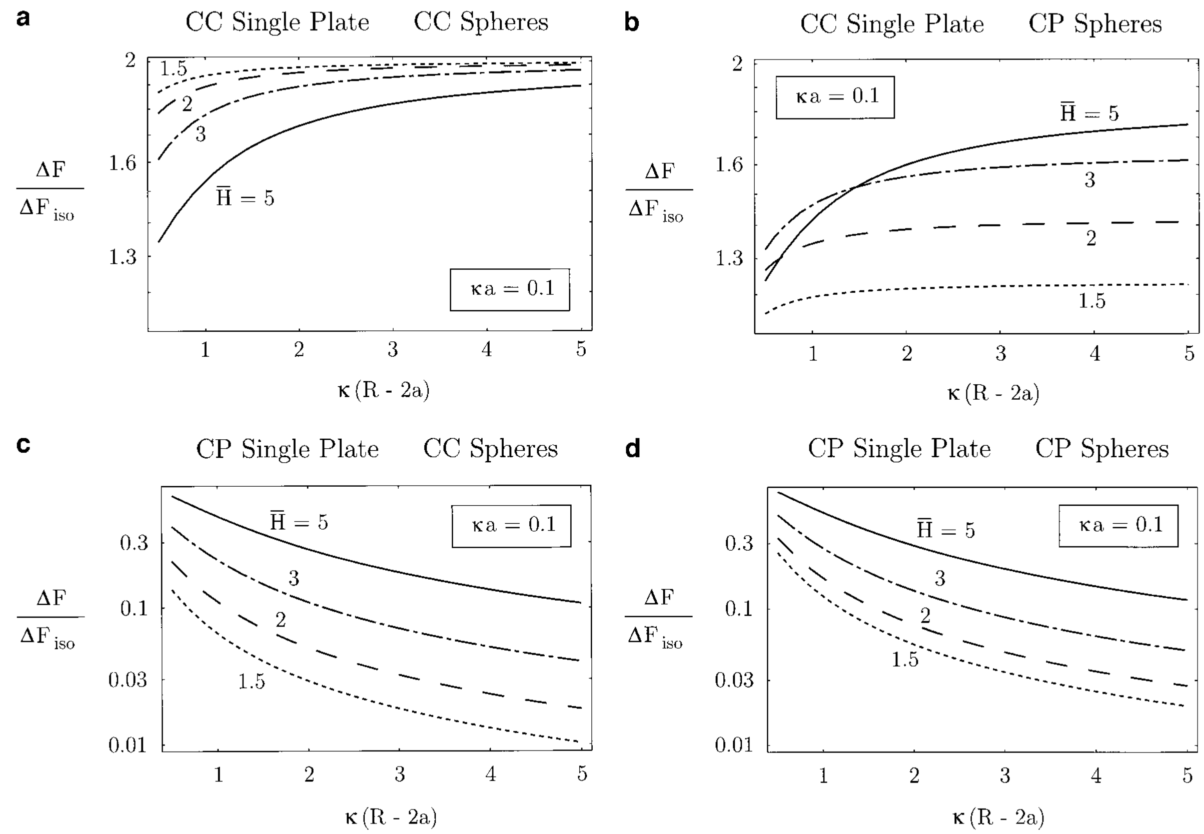

FIG. 3. Plot of ratio $\Delta F/\Delta F_{\mathrm{iso}}$, where ΔF is the interaction free energy for two spheres near a *single plate* and ΔF_{iso} is the interaction free energy for two spheres in an unbounded fluid (Eq. [8]). Results given for $\kappa a = 0.1$, isolated plate potential $\Phi_{\mathrm{p}}^{\mathrm{iso}} = 0$, and normalized sphere–plate separations $\bar{H} = H/2a$: $\bar{H} = 1.5$ (short dashed line), $\bar{H} = 2$ (dashed line), $\bar{H} = 3$ (short-long dashed line), and $\bar{H} = 5$ (solid line). (a) CC spheres and CC plate, (b) CP spheres and CC plate, (c) CC spheres and CP plate, (d) CP spheres and CP plate.

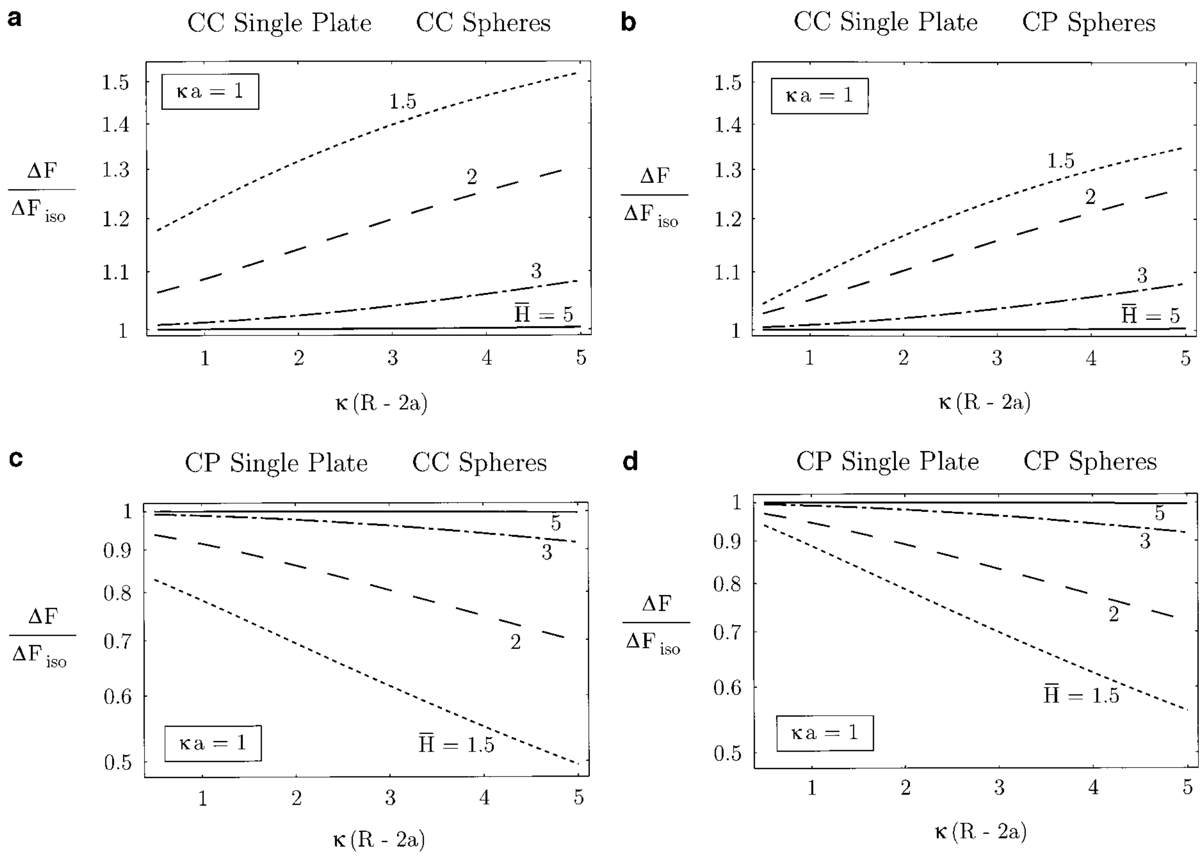

FIG. 4. As for Fig. 3 but for $\kappa a = 1$.

In all cases, we observe that $\Phi_{\rm eff}$ and hence the interaction can vanish only if the following conditions are satisfied: (i) for CP spheres, for which $\Gamma > 0$, the isolated surface potentials of the spheres $\Phi_s^{\rm iso}$ and the plate(s) $\Phi_p^{\rm iso}$ must have the same sign, whereas for (ii) CC spheres, for which $\Gamma < 0$, these isolated surface potentials must be opposite in sign. We shall discuss the implications of these findings further below.

3b. Separation Dependencies

The separation dependencies of the interaction free energy ΔF, namely, $g_1(R)$ for the single-plate case and $g_2(R)$ for the double-plate case, are both functions of the sphere–plate separation $(H/2)$. We note that in both cases the separation dependencies are strictly positive monotonically decreasing functions of R, indicating a repulsion, in line with Ref. (12). In Fig. 1 we present a comparison of the separation dependence for the single-plate case to the unconfined case, where it is evident that the effect of the CC plate is to increase the separation dependence between the spheres, whereas the CP plate will decrease the separation dependence. The amount in which the separation dependence is decreased or increased is strongly dependent on the normalized sphere–plate separation $(\kappa H/2)$ as well as the normalized sphere–sphere separation (R/H). Consequently, we observe that for $\kappa H < O(1)$, the separation dependence is modified significantly provided $(R/H) > O(1)$, whereas for $\kappa H > O(1)$ the separation dependence is modified if $(R/H) > O(\kappa H)$. For the CC plate case, the separation dependence relative to the unconfined case [8] can be doubled by the presence of the plate, whereas for the CP plate the separation dependence can be dramatically reduced. All these properties can be easily understood by considering the presence and signs of the image charges in both cases.

For the case of two spheres confined between two plates, we would expect that the effects discussed above for the single-plate case would be enhanced. In Fig. 2 we present results for the two-plate case. In contrast to the single CC plate case, in which the separation dependence relative to the unconfined case was at most doubled, the enhancement in the two-plate case is unbounded. From Figs. 1b and 2b, we see that for the CP plates, the decrease in the separation dependence for the two-plate case is much more pronounced than in the single-plate case. Also, from [7] it is evident that the "effective Debye length" in the double CP plate case is modified from the unconfined result. To quantify this, we observe that for large separations $R \gg H$, $g_2(R) \sim (4/H)K_0(\kappa R\sqrt{1 + (\pi/[\kappa H])^2})$ for CP plates, whereas $g_2(R) \sim (2/H)K_0(\kappa R)$ for CC plates. Noting the asymptotic form of $K_0(x) \sim \sqrt{\pi/(2x)}e^{-x}$, for large x, it is then clear that for the CP plate case, the effective Debye length $\kappa_{\rm eff}^{-1}$ is

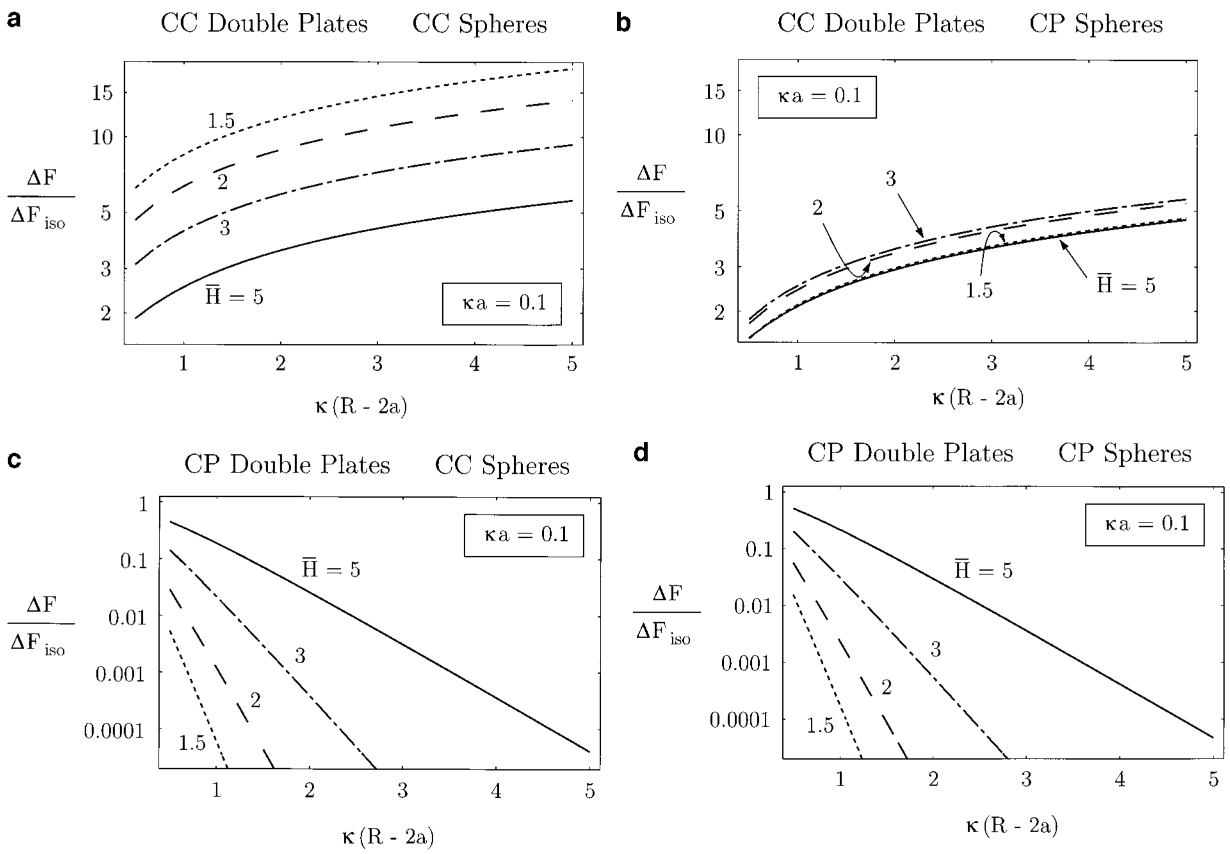

FIG. 5. Plot of ratio $\Delta F/\Delta F_{\mathrm{iso}}$, where ΔF is the interaction free energy for two spheres confined between *two plates* and ΔF_{iso} is the interaction free energy for two spheres in an unbounded fluid (Eq. [8]). Results given for $\kappa a = 0.1$, isolated plate potential $\Phi_p^{\mathrm{iso}} = 0$, and normalized sphere–plate separations $\bar{H} = H/2a$: $\bar{H} = 1.5$ (short dashed line), $\bar{H} = 2$ (dashed line), $\bar{H} = 3$ (short-long dashed line), and $\bar{H} = 5$ (solid line). (a) CC spheres and CC plates, (b) CP spheres and CC plates, (c) CC spheres and CP plates, (d) CP spheres and CP plates.

$$\kappa_{\mathrm{eff}} = \kappa\sqrt{1 + (\pi/[\kappa H])^2}, \qquad [11]$$

which is dependent on the normalized sphere–plate separation $(\kappa H/2)$.[2] In contrast, the interaction is modified only by a weak algebraic $R^{1/2}$ type behavior for confinement between CC plates.

3c. Interaction Free Energies

We now examine the combined effects of the separation dependencies $g_1(R)$, $g_2(R)$ and the effective potential Φ_{eff} on the interaction free energy $\Delta F(R)$, henceforth simply referred to as the *interaction*. Our discussion shall be restricted to cases for which the interaction is significantly affected by confinement, namely, $\kappa a < O(1)$. We note that for larger values of κa, the interaction can be greatly affected by confinement, although this will occur at sphere–sphere separations where the interaction is negligibly small.

i. Single plate: Zero isolated potential $\Phi_p^{\mathrm{iso}} = 0$. First, we investigate the interaction of two charged spheres in the vicinity of a single plate carrying zero isolated potential, i.e., $\Phi_p^{\mathrm{iso}} = 0$. Note that the plate can be held at a constant surface charge density (CC) or constant surface potential (CP). In Fig. 3 we present results for $\kappa a = 0.1$ and for various sphere–plate separations and electrical boundary conditions on the spheres and plate. From Figs. 3a and 3b it is evident that the interaction of two CC spheres in the vicinity of a single CC plate differs considerably from that of two CP spheres in the vicinity of the same plate. In particular, we note that as the CC spheres are brought closer to the plate, the interaction is enhanced. For CP spheres, however, if $\kappa(R - 2a) \gtrsim 1.5$ then there is a reduction in the interaction as the normalized sphere–plate separation $H/2a$ is reduced from 5; otherwise the interaction increases, reaches a maximum, and then decreases as the spheres are brought closer to the plate. This unusual behavior can be understood by noting that $\Gamma = -3 \times 10^{-3}$ for the CC spheres, whereas $\Gamma = 1.002$ for the CP spheres. From [4b], it then follows that the effective potential Φ_{eff} is virtually unaffected by the plate if the spheres are of the CC type, whereas for CP spheres, Φ_{eff} decreases considerably with decreasing sphere–plate separation. Consequently, the increase in the interaction observed in Fig. 3a for the CC spheres is due primar-

[2] Recent numerical calculations of the interaction of two identical charged cylinders confined between two constant potential plates also show a reduction in the effective Debye screening length upon confinement. See Ref. (20).

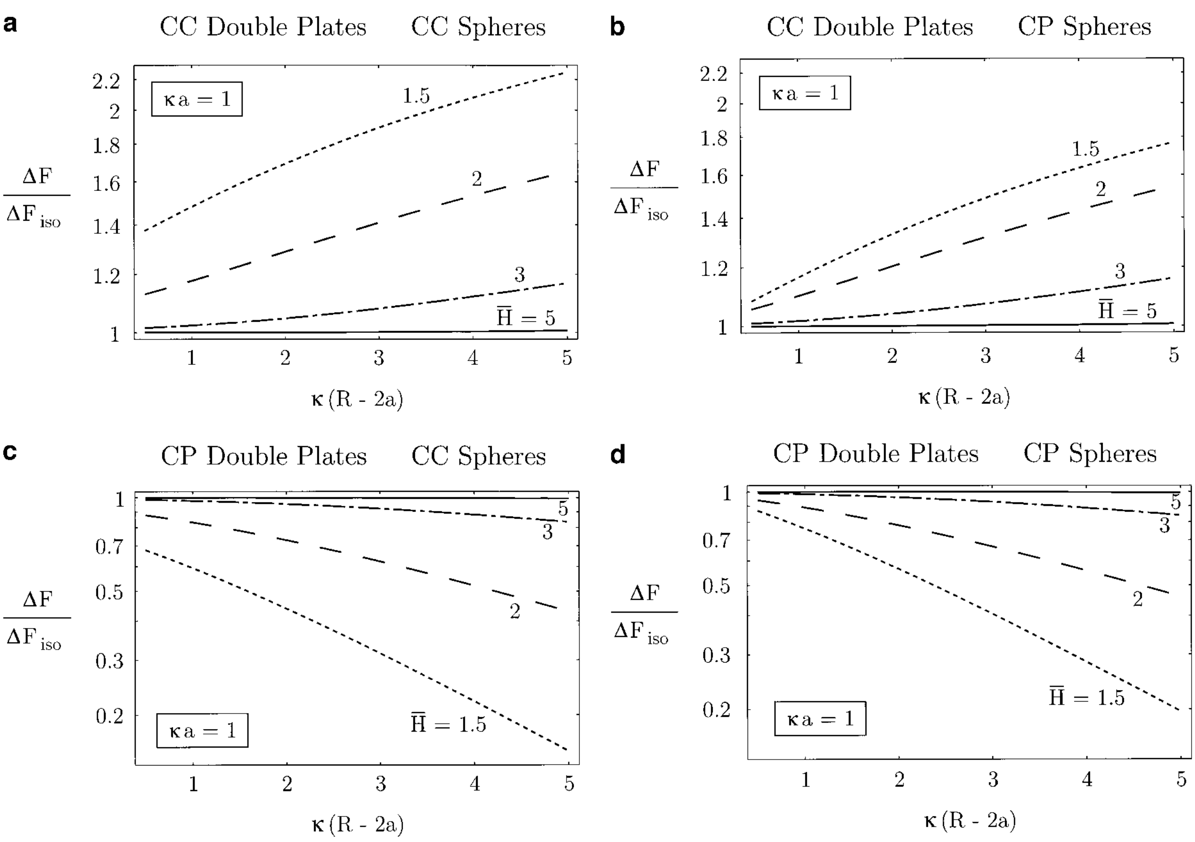

FIG. 6. As for Fig. 5 but for $\kappa a = 1$.

ily to the enhancing effects of the separation dependence $g_1(R)$ (see Fig. 1a), and the complex behavior observed in Fig. 3b for the CP spheres is due to the competing effects of Φ_{eff} and $g_1(R)$. In this latter case, Φ_{eff} is clearly the dominant mechanism that influences the interaction, if $\kappa(R - 2a) \gtrsim 1.5$.

Next we examine cases where the spheres are in the vicinity of a single CP plate, with $\Phi_{\mathrm{p}}^{\mathrm{iso}} = 0$. As discussed above, the separation dependence $g_1(R)$ in this case will tend to reduce the interaction, as the sphere–plate separation is decreased (see Fig. 1b). This behavior is borne out in Figs. 3c and 3d, for $\kappa a = 0.1$, where a significant reduction in the interaction is observed as the sphere–plate separation is reduced. Again we note that for CC spheres, $\Phi_{\mathrm{eff}} \cong \Phi_{\mathrm{s}}^{\mathrm{iso}}$ at all sphere–plate separations considered; whereas for the CP spheres, Φ_{eff} increases as the sphere–plate separation decreases. This explains the difference between the CC sphere interactions given in Fig. 3c and the CP sphere interactions in Fig. 3d. However, unlike the CC plate results in Figs. 3a and 3b, the separation dependence $g_1(R)$ dominates the interaction here.

In Fig. 4 we present analogous results for cases where $\kappa a = 1$, which corresponds to stronger screening of the particles and plate by the surrounding electrolyte. This enhanced screening also weakens the dependence of Φ_{eff} on the sphere–plate separation. From Figs. 4a and 4b it is evident that the interaction for two CC spheres and two CP spheres in the vicinity of a single uncharged CC plate are qualitatively similar; a reduction in the sphere–plate separation results in an increase in the interaction between the spheres. Again we note that $\Phi_{\mathrm{eff}} \cong \Phi_{\mathrm{s}}^{\mathrm{iso}}$ for CC spheres; whereas for CP spheres the effective potential Φ_{eff} is significantly affected by the plate. These properties explain the reduction in the interaction for the CP spheres (see Fig. 4b), in comparison with the interaction of the CC spheres (see Fig. 4a). In Figs. 4c and 4d we give the corresponding results for a single CP plate. Here we note that the separation dependence $g_1(R)$ will tend to reduce the interaction in comparison to its value when the particles are unconfined, and this is borne out in the results. Again the difference between the interaction of the CC and CP spheres is due to the differing behavior of Φ_{eff} in both cases, as discussed above.

ii. Two plates: Zero isolated potential $\Phi_{\mathrm{p}}^{\mathrm{iso}} = 0$. We now present results for the case where the spheres are confined between two plates, both of which have zero isolated potential, i.e., $\Phi_{\mathrm{p}}^{\mathrm{iso}} = 0$, and examine the effects of different boundary conditions on the spheres and plates. Here we expect similar, yet enhanced, behavior to that found for the single-plate case discussed above. In Fig. 5 we present results for $\kappa a = 0.1$. For the case of confinement by CC plates we find that the interaction between two CC spheres is enhanced greatly by the presence of the plates (see Fig. 5a). A reduction in the sphere–plate separation increases the interaction between the spheres. For two CP spheres confined between CC plates (see Fig. 5b), however, we observe that the interaction

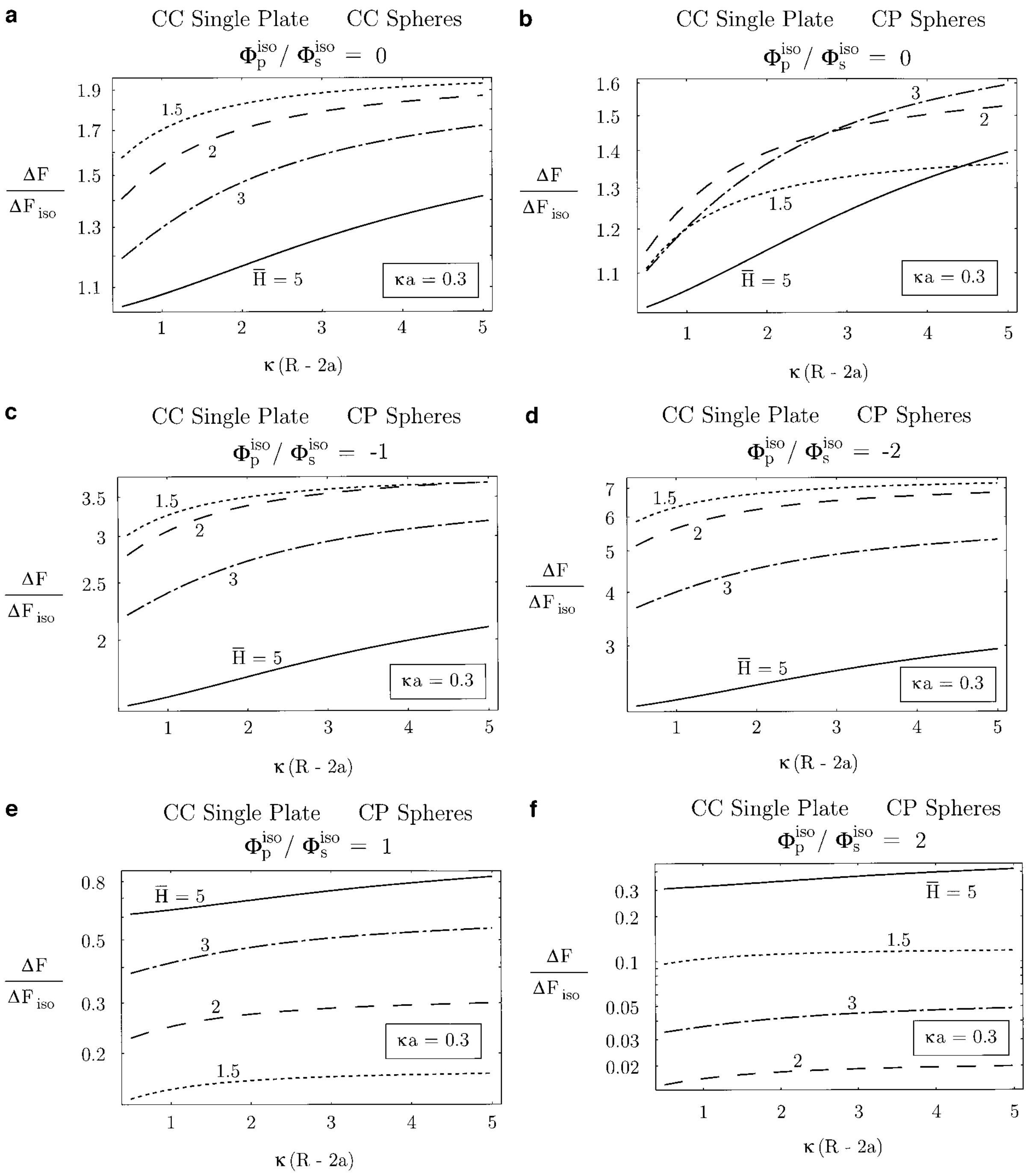

FIG. 7. Plot of ratio $\Delta F/\Delta F_{\mathrm{iso}}$, where ΔF is the interaction free energy for two spheres near a *single CC plate* and ΔF_{iso} is the interaction free energy for two spheres in an unbounded fluid (Eq. [8]). Results given for $\kappa a = 0.3$ and normalized sphere–plate separations $\bar{H} = H/2a$: $\bar{H} = 1.5$ (short dashed line), $\bar{H} = 2$ (dashed line), $\bar{H} = 3$ (short-long dashed line), and $\bar{H} = 5$ (solid line). (a) CC spheres and $\Phi_p^{\mathrm{iso}}/\Phi_s^{\mathrm{iso}} = 0$, (b) CP spheres and $\Phi_p^{\mathrm{iso}}/\Phi_s^{\mathrm{iso}} = 0$, (c) CP spheres and $\Phi_p^{\mathrm{iso}}/\Phi_s^{\mathrm{iso}} = -1$, (d) CP spheres and $\Phi_p^{\mathrm{iso}}/\Phi_s^{\mathrm{iso}} = -2$, (e) CP spheres and $\Phi_p^{\mathrm{iso}}/\Phi_s^{\mathrm{iso}} = 1$, (f) CP spheres and $\Phi_p^{\mathrm{iso}}/\Phi_s^{\mathrm{iso}} = 2$.

increases, reaches a maximum, and then decreases as the sphere–plate separation is reduced. In particular, note that for $H/2a = 1.5$ and 5, the interactions are almost identical for all sphere–sphere separations. This rich and complex behavior observed with the CP spheres is again due to the competing effects of Φ_{eff} and $g_2(R)$. Also note that the interaction $\Delta F(R)$ is markedly lower for CP spheres in comparison to the results for CC spheres, yet it is considerably higher than the unconfined interaction free energy.

In Figs. 5c and 5d we present results corresponding to confinement between two CP plates, for $\kappa a = 0.1$. Note the dramatic reduction in the interaction between the spheres in comparison to the unconfined interaction, for both CC and CP spheres. The reduction in the effective Debye length, as discussed above, is clearly evident in these results. We also point out that the reduction in the interaction for the CC spheres is primarily due to $g_2(R)$, whereas Φ_{eff} has a significant effect only for the CP spheres; the interaction between the CP spheres is greater than that of the CC spheres, especially for small sphere–plate separations.

In Fig. 6 results are given for confinement by two plates, for $\kappa a = 1$. Again similar results are found to the single-plate case (see Fig. 4), although the influence of the two plates is greater. Also note that the effects of Φ_{eff} and $g_2(R)$ are diminished in comparison to the $\kappa a = 0.1$ double-plate case, due to the stronger screening of the electrolyte.

iii. Nonzero isolated potentials $\Phi_{\text{p}}^{\text{iso}}$. We now examine the effect of nonzero isolated surface potential $\Phi_{\text{p}}^{\text{iso}}$ on the confining plate. Results for single-plate confinement only will be presented, since results for the double-plate case exhibit similar qualitative trends. Furthermore, we shall restrict our discussion to plates of the CC type, since this will serve to adequately illustrate the important features of the interaction for nonzero isolated plate potentials. In Fig. 7 we present results for $\kappa a = 0.3$, where the plates are of the CC type. Importantly, we note that for the CC spheres, Φ_{eff} is only weakly affected by the presence of the plate for reasonable choices of $\Phi_{\text{p}}^{\text{iso}}/\Phi_{\text{s}}^{\text{iso}}$; i.e., $\Phi_{\text{eff}} \cong \Phi_{\text{s}}^{\text{iso}}$ unless $|\Phi_{\text{p}}^{\text{iso}}| \gg |\Phi_{\text{s}}^{\text{iso}}|$, since $\Gamma = -0.023$ here. Consequently, the only results presented for the interaction of two CC spheres are for a plate held at $\Phi_{\text{p}}^{\text{iso}} = 0$ (see Fig. 7a). These results exhibit similar behavior to those discussed above in Figs. 3a and 4a. In Fig. 7b we present corresponding results for the interaction of two CP spheres in the vicinity of a CC plate with $\Phi_{\text{p}}^{\text{iso}} = 0$. Here the effective potential Φ_{eff} is strongly dependent on the sphere–plate separation which, when combined with the enhancing effects of $g_1(R)$, results in the complex behavior observed. We now examine the influence of varying the isolated plate potential $\Phi_{\text{p}}^{\text{iso}}$. Noting that $\Gamma > 1$, it is clear from [4b] that as the isolated potential ratio $\Phi_{\text{p}}^{\text{iso}}/\Phi_{\text{s}}^{\text{iso}}$ is made increasingly negative, then $\Phi_{\text{eff}}/\Phi_{\text{s}}^{\text{iso}}$, and hence the interaction between the spheres, will increase. This effect is demonstrated in Figs. 7c and 7d for $\Phi_{\text{p}}^{\text{iso}}/\Phi_{\text{s}}^{\text{iso}} = -1$ and -2. However, if $\Phi_{\text{p}}^{\text{iso}}/\Phi_{\text{s}}^{\text{iso}}$ is made increasingly positive, $\Phi_{\text{eff}}/\Phi_{\text{s}}^{\text{iso}}$ will decrease. In particular, for a critical value of $\Phi_{\text{p}}^{\text{iso}}/\Phi_{\text{s}}^{\text{iso}}$, at a fixed sphere–plate separation, Φ_{eff} will vanish, resulting in zero interaction between the spheres. Consequently, as $\Phi_{\text{p}}^{\text{iso}}/\Phi_{\text{s}}^{\text{iso}}$ is increased from zero for a given sphere–plate separation, the interaction between the spheres will decrease, vanish, and then increase. This behavior is borne out in Figs. 7e and 7f for $\Phi_{\text{p}}^{\text{iso}}/\Phi_{\text{s}}^{\text{iso}} = 1$ and 2. For $\Phi_{\text{p}}^{\text{iso}}/\Phi_{\text{s}}^{\text{iso}} = 1$ (see Fig. 7e), we observe that the interaction between the spheres decreases with decreasing sphere–plate separation, results that are reminiscent of confinement by a CP plate (see Figs. 3d and 4d). However, unlike the CP plate case, this reduction in the interaction is due to Φ_{eff}. In Fig. 7f we see that for $\Phi_{\text{p}}^{\text{iso}}/\Phi_{\text{s}}^{\text{iso}} = 2$, the interaction between the spheres decreases and then increases as the sphere–plate separation is reduced. This interesting behavior is due to the interaction vanishing at a separation $H/2a = 2.36$ (evaluated from Eq. [9]). We note that for larger values of $\Phi_{\text{p}}^{\text{iso}}/\Phi_{\text{s}}^{\text{iso}}$, we will again find that the interaction between the spheres increases monotonically as the sphere–plate separation is reduced.

TABLE 1
Values of $\Phi_{\text{p}}^{\text{iso}}/\Phi_{\text{s}}^{\text{iso}}$ for which $\Phi_{\text{eff}} = 0$ at Different Sphere–Plate Separations $H/2a$

$\frac{H}{2a}$	$\frac{\Phi_{\text{p}}^{\text{iso}}}{\Phi_{\text{s}}^{\text{iso}}}$ CP spheres	$\frac{\Phi_{\text{p}}^{\text{iso}}}{\Phi_{\text{s}}^{\text{iso}}}$ CC spheres
1.5	1.55	−67.4
2	1.80	−78.3
3	2.42	−106
5	4.42	−193

Note. CC and CP spheres are in the vicinity of a single plate.

TABLE 2
Values of $\Phi_{\text{p}}^{\text{iso}}/\Phi_{\text{s}}^{\text{iso}}$ for which $\Phi_{\text{eff}} = 0$ at Different Sphere–Plate Separations $H/2a$

	$\frac{\Phi_{\text{p}}^{\text{iso}}}{\Phi_{\text{s}}^{\text{iso}}}$			
	CC plates		CP plates	
$\frac{H}{2a}$	CP spheres	CC spheres	CP spheres	CC spheres
1.5	1.09	−47.4	0.46	−20.0
2	1.17	−50.9	0.63	−27.3
3	1.41	−61.5	1.01	−44.1
5	2.32	−101	2.10	−91.4

Note. CC and CP spheres are confined between two CC and CP plates.

iv. Condition for zero interaction. Finally, we quantify the values of $\Phi_{\text{p}}^{\text{iso}}/\Phi_{\text{s}}^{\text{iso}}$ for which the effective potential Φ_{eff}, and hence the interaction free energy $\Delta F(R)$, vanishes. In Table 1 we present results for confinement by a single plate, for $\kappa a = 0.3$. We note that these results do not depend on the electrical nature of the plate, but only on the sphere properties, as is evident from [9]. From Table 1 it is clear that for two CP spheres, $\Delta F(R)$ vanishes at practically achievable values of $\Phi_{\text{p}}^{\text{iso}}/\Phi_{\text{s}}^{\text{iso}}$. These results contrast with those for CC spheres, where highly unreasonable values of $\Phi_{\text{p}}^{\text{iso}}/\Phi_{\text{s}}^{\text{iso}}$ must be obtained. Similar results are also found for confinement between two plates, see Table 2. However, in contrast to the single-plate case, these results depend on the electrical nature of the confining plates. For the interaction of two CP spheres, we again observe that the interaction can vanish at practically achievable values of $\Phi_{\text{p}}^{\text{iso}}/\Phi_{\text{s}}^{\text{iso}}$, whereas the same cannot be said for the CC sphere case.

4. CONCLUSIONS

The double-layer interaction between two spherical particles immersed in an unbounded electrolyte has been extensively investigated by many workers. In this paper, we examined the proximity effects of one or two charged plates on the pairwise double-layer interaction between two identical spherical particles. We found that the proximity of one or two flat plates can dramatically affect this pairwise interaction, resulting in a reduction, enhancement, or elimination of the interaction, this behavior being strongly dependent on the electrical properties of the spheres and that of the confining plate(s). In particular, we found that the interaction between two confined CC spheres is primarily affected by the electrical nature of the confining plate(s), whereas the charge or potential of the plate(s) exerts only a weak influence. This contrasts with the interaction between two CP spheres which is strongly affected by both the potential/charge and the electrical properties of the confining plate(s). These findings indicate that greater control and modification of the pairwise interaction is achievable in practice for CP spheres in comparison to CC spheres.

ACKNOWLEDGMENTS

This research was supported by the Advanced Minerals Products Centre of the Australian Research Council and by the Australian Research Council Grants scheme.

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