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Accurate Analytic Formulas for the Double-Layer Interaction between Spheres

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Very simple but accurate analytic formulas are presented for the electrical double-layer force and interaction free energy between two spherical colloidal particles, valid up to the moderate- to high-potential regime. These formulas represent a remarkable improvement on previous analytic and semianalytic formulas for the interaction, while maintaining an excellent degree of analytic simplicity. Furthermore, a detailed derivation of the interaction free energy between two dissimilar spheres in the linear Debye–Huckel approximation is presented that is valid for all κh, where κ is the Debye screening parameter and h is the distance of closest approach between the spheres. In doing so, it is demonstrated that the well-known Hogg–Healy–Fuersteneau (HHF) formula, which is valid only in the small κh regime, may be trivially modified to extend its range of applicability to all κh.

INTRODUCTION

In many applications of colloid and surface science, it is desirable to have simple yet accurate expressions for the electrical double-layer interaction between particles that are valid over a reasonably large range of surface potentials and particle separations. In this paper, we present results that fulfill this role.

The derivation of our results begins with the treatment of the double-layer interaction based on the linear Debye–Huckel equation for two dissimilar spheres. We follow the method of Bell *et al.* (1) and obtain simple and accurate analytic expressions for the force and interaction free energy for this model. Accurate numerical solutions for this problem are available via an eigenfunction expansion method (2–4), and these are used as benchmarks to determine the accuracy of our formulas. Our results are more accurate than the Derjaguin approximation over a large range of particle sizes as well as surface separations and surface potential asymmetries. Furthermore, through our analysis we demonstrate that the original Derjaguin approximation, which is valid only for small separations, may be trivially modified to encompass all separations.

With the knowledge gained from the study of the linear Debye–Huckel model, we then present a generalization of the above-mentioned low-potential result to encompass the moderate- to high-potential regime. As we shall demonstrate and discuss, our results present a remarkable improvement over previous analytic and semianalytic formulas (1) for the interaction between identical spheres with large surface potentials. Our benchmark for this calculation comes from our numerical solution of the nonlinear Poisson–Boltzmann (NLPB) equation for two spheres (5).

We note that all results presented in this paper are derived under the assumption of constant potential at the particle surfaces.

LINEAR THEORY FOR TWO SPHERES

In this section, we develop a simple analytic solution for the double-layer interaction between two dissimilar spheres at constant surface potential in the linear Debye–Huckel approximation, where the potential ψ satisfies the equation

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

and κ is the Debye screening parameter. The derivation relies on κa (a is the sphere radius) being large, which is the regime where the Derjaguin method for deriving the interaction between curved surfaces from a knowledge of the interaction between parallel plates is expected to be applicable. This is of course provided that the radii of curvature of the surfaces greatly exceed the minimum separation between them (1). When the Derjaguin approximation is applied to the two-sphere problem in the linear Debye–Huckel theory, the result is referred to as the Hogg–Healy–Fuersteneau (HHF) formula (6). For later reference, we call our present approach the modified HHF approximation. The HHF approximation is accurate for large κa and small κh (h is the distance of closest approach between the spheres) as discussed above, but as we shall see the modified HHF approximation presented here is accurate even for modest κa values and for all ranges of κh of practical interest.

The modified HHF result is based on the original integral equation formulation of Bell *et al.* (1), who showed that by

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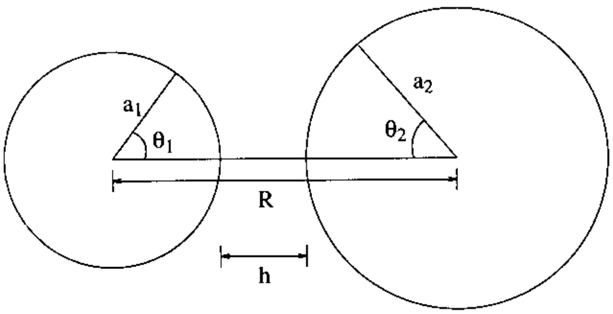

FIG. 1. Geometry of two interacting dissimilar spheres.

considering the dipole moment distribution around each sphere via an approximate integral equation formulation, the interaction free energy can be directly obtained. The resulting expression given by Bell *et al.* for the interaction free energy is, however, considerably more complex than the HHF approximation. In this paper we rework the analysis of Bell *et al.* (1) and obtain an expression for the interaction free energy that possesses a remarkable resemblance to the original HHF expression with a very slight modification. We emphasize that the formula we present here and that given by Bell *et al.* for the interaction free energy possess similar accuracies, and both present a significant improvement on the original HHF formula. Thus, the modified HHF result given here has accuracy similar to that of the result of Bell *et al.*, yet retains the analytic simplicity of the HHF formula. Accurate analytic corrections to the HHF formula are also available (7); however, the final expressions are still relatively complex.

Using the Green's function method (8), Bell *et al.* (1) showed that the Debye–Huckel equation can be transformed into two coupled integral equations for the dipole moment functions $\mu_1(\mathbf{P}_1)$ and $\mu_2(\mathbf{P}_2)$ around spheres 1 and 2, respectively, namely,

$$\Psi_1 = -2\pi\mu_1(\mathbf{P}_1) + a_1^2 \int_{S_1} \mu_1(\mathbf{P}'_1)\nabla G(\mathbf{P}_1, \mathbf{P}'_1)\cdot\hat{\mathbf{n}}_1 dS' + a_2^2 \int_{S_2} \mu_2(\mathbf{P}'_2)\nabla G(\mathbf{P}_1, \mathbf{P}'_2)\cdot\hat{\mathbf{n}}_2 dS', \quad [2]$$

where the second integral equation is obtained by interchanging the subscripts 1 and 2. Note that subscripts 1 and 2 indicate whether the function refers to sphere 1 or 2, respectively. Also, variables under integral signs that are primed (e.g., $\mathbf{P}'_1$) are variables of integration. With this notation in mind, we now define all variables in the integral equation [2]: Ψ is the surface potential on the sphere; a is the radius of the sphere; $\mathbf{P}$ is a point on the surface of the sphere; S refers to the surface of the sphere; $\hat{\mathbf{n}}$ is the inward normal unit vector to the surface of the sphere, i.e., toward the center of the sphere; and $G(\mathbf{P}, \mathbf{P}')$ is the Green's function:

$$G(\mathbf{P}, \mathbf{P}') = \frac{e^{-\kappa|\mathbf{P}-\mathbf{P}'|}}{|\mathbf{P}-\mathbf{P}'|}. \quad [3]$$

Bell *et al.* (1) then defined the perturbations $\Delta\mu_1(\mathbf{P}_1)$ and $\Delta\mu_2(\mathbf{P}_2)$ to the dipole moment functions as

$$\mu_1(\mathbf{P}_1) = \mu_1^0 + \Delta\mu_1(\mathbf{P}_1), \quad [4a]$$

$$\mu_2(\mathbf{P}_2) = \mu_2^0 + \Delta\mu_2(\mathbf{P}_2), \quad [4b]$$

where μ_1^0 and μ_2^0 are the dipole moment distributions around spheres 1 and 2, respectively, if the spheres were individually taken in isolation.

From the natural symmetry of the two spheres, it is clear that $\mu_1(\mathbf{P}_1)$ and $\mu_2(\mathbf{P}_2)$ only depend on the angles θ_1 and θ_2, respectively (see Fig. 1), as was discussed in (1). Using this fact, and from [2] and [4], Bell *et al.* then obtained the following approximate expressions for $\Delta\mu_1$ and $\Delta\mu_2$:

$$2\pi u(\kappa a_1)\Delta\mu_1(\theta_1) = \frac{S_1\Psi_2 - S_1S_2\Psi_1}{1 - S_1S_2}, \quad [5a]$$

$$2\pi u(\kappa a_2)\Delta\mu_2(\theta_2) = \frac{S_2\Psi_1 - S_1S_2\Psi_2}{1 - S_1S_2}. \quad [5b]$$

Here,

$$S_1 = \frac{a_2}{b_1} e^{-\kappa(b_1 - a_2)}, \quad [6a]$$

$$S_2 = \frac{a_1}{b_2} e^{-\kappa(b_2 - a_1)}, \quad [6b]$$

$$b_1^2 = a_1^2 + R^2 - 2a_1R\cos\theta_1, \quad [6c]$$

$$b_2^2 = a_2^2 + R^2 - 2a_2R\cos\theta_2, \quad [6d]$$

$$u(x) = \frac{x - 1 + (x+1)e^{-2x}}{x}, \quad [6e]$$

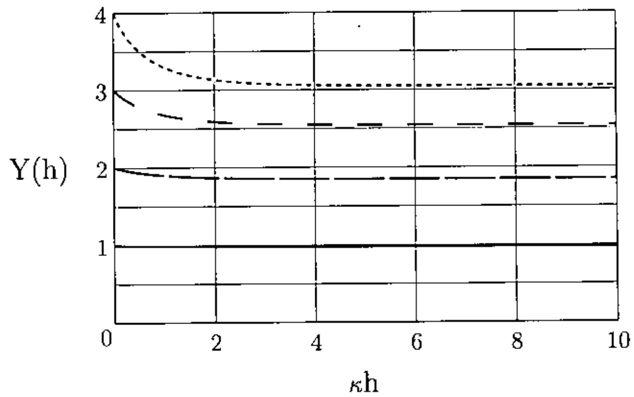

FIG. 2. The function $Y(h)$ defined in Eq. [16] for reduced surface potentials of $y_s = 1$ (bottom), 2, 3, and 4 (top).

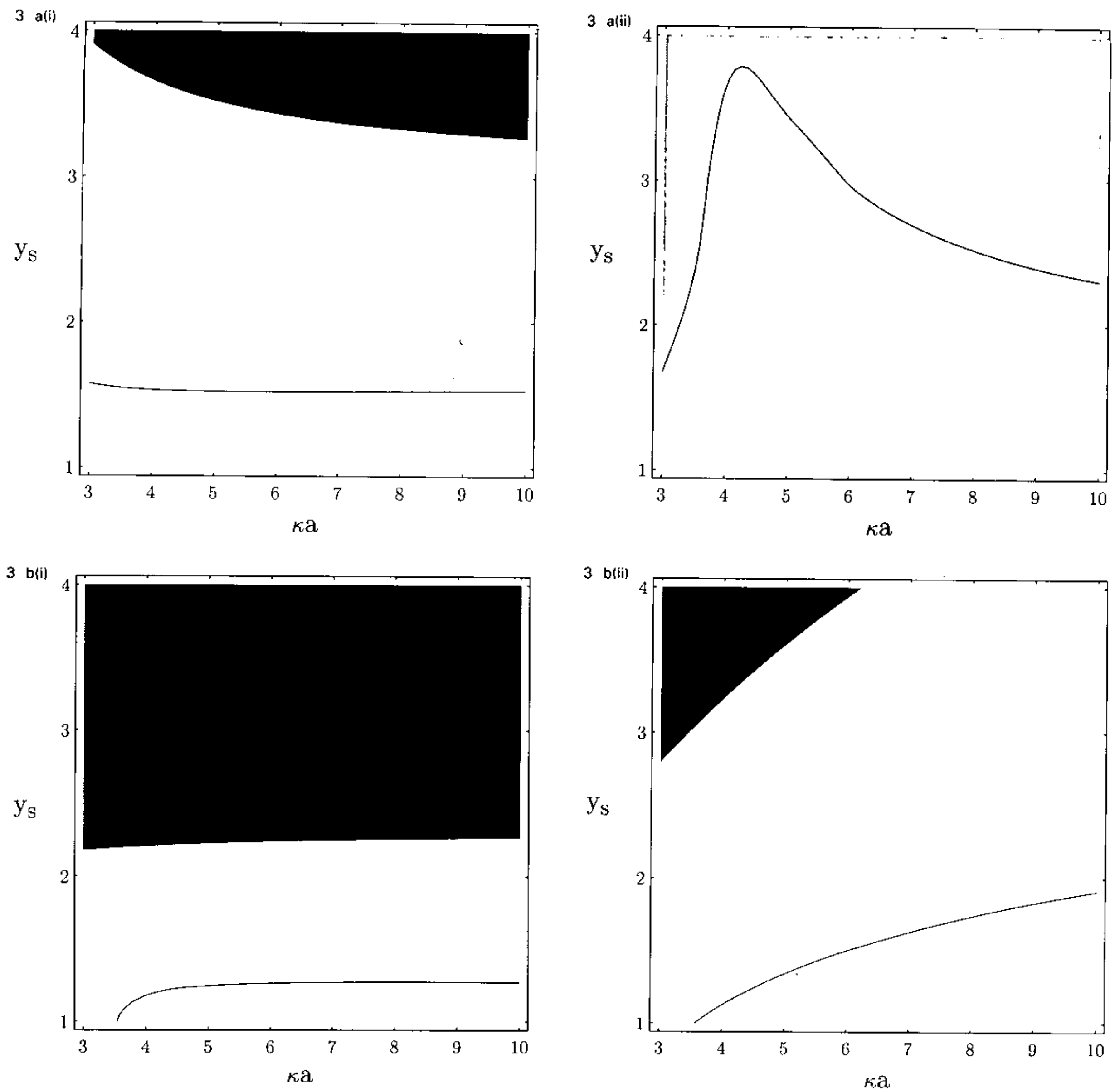

FIG. 3. Magnitude of the maximum relative error of the interaction free energy, in the particle radius κa and reduced surface potential y_s domain, for the interaction between two identical spheres at constant surface potential. In the white region the error is less than 3%, in the gray region less than 10%, and in the black region greater than 10%. (a) Interaction free energy according to [19b] for (i) $0.2 \leqslant \kappa h \leqslant 1$ and (ii) $1 \leqslant \kappa h \leqslant 2$; (b) interaction free energy according to [20b] for (i) $0.2 \leqslant \kappa h \leqslant 1$ and (ii) $1 \leqslant \kappa h \leqslant 2$; (c) interaction free energy according to V_{asym} for (i) $0.2 \leqslant \kappa h \leqslant 1$ and (ii) $1 \leqslant \kappa h \leqslant 2$.

and R is the distance between the centers of the spheres (see Fig. 1). Note that although the expressions for $\Delta\mu_1$ and $\Delta\mu_2$ given in [5] were derived in the small κh limit, i.e., $\kappa h \ll \kappa(a_1 + a_2)$, they in fact also possess the correct limiting forms for large κh.

We now present a modification to [5] that simplifies the expression considerably and yet retains the correct limiting forms for small and large κh. With the small κh limit imposed in the derivation of [5], and since for small κh we are concerned only with small angles θ_1 and θ_2, as discussed in (1), it is clear that [5] are well approximated by

$$2\pi u(\kappa a_1)\Delta\mu_1(\theta_1) = \frac{a_2}{b_1}\frac{(\Psi_2 - \Psi_1 e^{-\kappa(b_1-a_2)})e^{-\kappa(b_1-a_2)}}{1 - e^{-2\kappa(b_1-a_2)}}, \quad [7a]$$

$$2\pi u(\kappa a_2)\Delta\mu_2(\theta_2) = \frac{a_1}{b_2}\frac{(\Psi_1 - \Psi_2 e^{-\kappa(b_2-a_1)})e^{-\kappa(b_2-a_1)}}{1 - e^{-2\kappa(b_2-a_1)}}. \quad [7b]$$

Note that [7] possess the correct limiting forms for (i) small θ_1, θ_2, and κh and (ii) large κh. Since [5] was derived under these same limits, then clearly [5] and [7] can be considered as equivalent approximations.

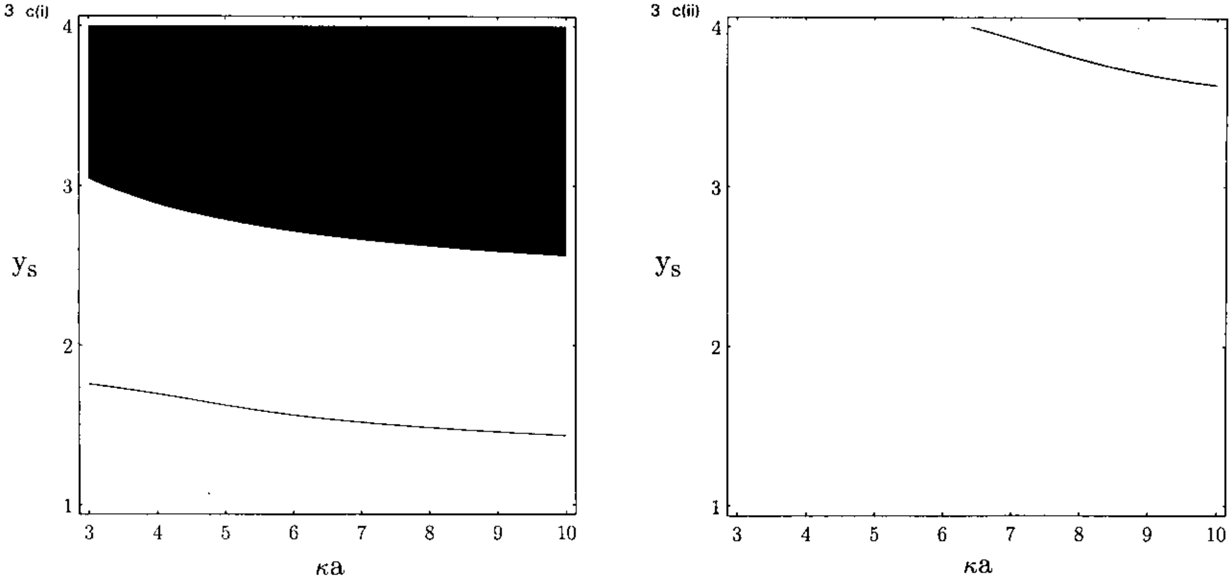

FIG. 3—*Continued*

Equations [7] may then be substituted directly into Eqs. [A.27] and [A.28] of (1) using [6c] and [6d], without any further assumptions or approximations, and then integrated analytically to give the following expression for the interaction free energy V between dissimilar spheres in the Debye–Huckel model:

$$V = \frac{\epsilon}{4}\left(\frac{kT}{e_0}\right)^2 \frac{a_1 a_2}{R}\,[(y_1 + y_2)^2 \ln(1 + e^{-\kappa h}) + (y_1 - y_2)^2 \ln(1 - e^{-\kappa h})] \quad \text{"modified HHF."} \quad [8]$$

Here, k is Boltzmann's constant, T is the absolute temperature, e_0 is the proton charge, ϵ is the permittivity of the solution surrounding the spheres, and y_1 and y_2 are the reduced surface potentials [i.e., scaled by (kT/e_0)] on spheres 1 and 2, respectively. We call [8] the modified HHF formula and this is one of the key results of this paper that describes the interaction between two dissimilar spheres in the linear Debye–Huckel treatment.

Compared with the HHF formula (6),

$$V = \frac{\epsilon}{4}\left(\frac{kT}{e_0}\right)^2 \frac{a_1 a_2}{a_1 + a_2}\,[(y_1 + y_2)^2 \ln(1 + e^{-\kappa h}) + (y_1 - y_2)^2 \ln(1 - e^{-\kappa h})] \quad \text{"HHF,"} \quad [9]$$

we immediately see that [8] can be directly obtained from [9] with the simple substitution

$$\frac{a_1 a_2}{a_1 + a_2} \rightarrow \left(\frac{a_1 a_2}{a_1 + a_2 + h} = \frac{a_1 a_2}{R}\right). \quad [10]$$

Note that for small κh, the modified HHF result [8] coincides with the HHF formula [9]; and for large κh the modified HHF result [8] reduces to the linear superposition approximation (1), as does the formula of Bell *et al.* (1). A numerical assessment of the accuracy of the modified HHF result [8] is given under Results.

EXTENSION TO HIGH SURFACE POTENTIALS FOR IDENTICAL SPHERES

We now present the derivation of the extension of the low-potential modified HHF approximation [8] to the moderate- to high-potential regime ($\leq$100 mV), for the case of two identical spheres.

We begin by noting that Levine (9) showed that the solution to the NLPB equation for a single isolated sphere, in the large κa limit, is given by

$$y(r) \sim \frac{4a}{r}\tanh^{-1}\left[e^{-\kappa(r-a)}\tanh\left(\frac{y_s}{4}\right)\right], \quad [11]$$

where a is the radius of the sphere, y is the reduced potential, y_s is the reduced surface potential, and r is the distance from the center of the sphere.

We now consider the two-identical-sphere case and assume we are in a regime where the superposition approximation holds. The solution to the NLPB equation for this case is then given by the sum of two terms similar to that in [11],

$$y(r_1) \sim \frac{a}{r_1} Y_1(r_1) e^{-\kappa(r_1 - a)} + \frac{a}{r_2} Y_2(r_2) e^{-\kappa(r_2 - a)}, \quad [12]$$

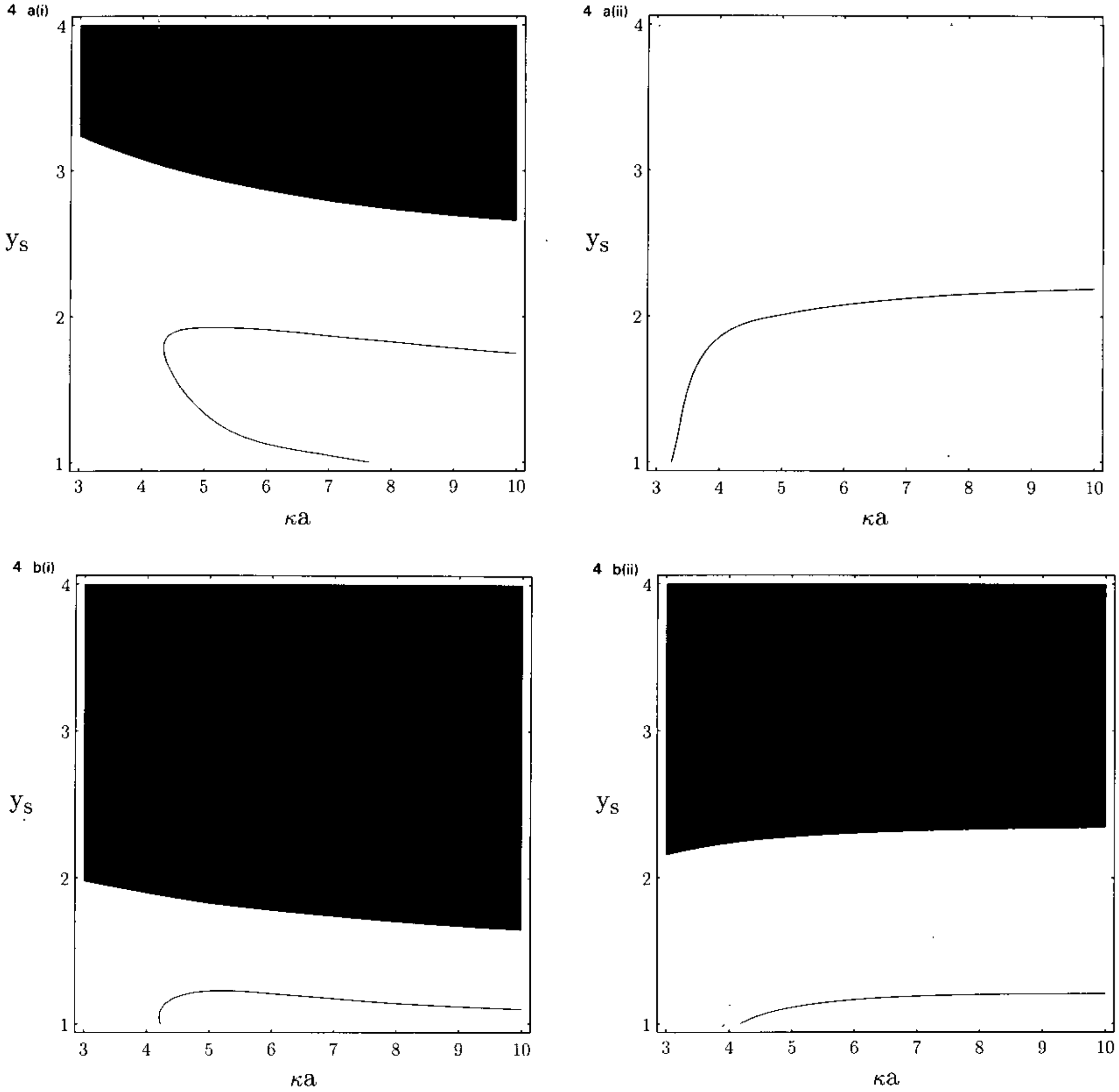

FIG. 4. As for Fig. 3 but comparing (a) [19a], (b) [20a], and (c) $\tilde{F}_{\text{asym}}$ for the force between two identical spheres.

where the functions Y_1 and Y_2 are given by

$$Y_1(r_1) = 4e^{\kappa(r_1-a)}\tanh^{-1}\left[e^{-\kappa(r_1-a)}\tanh\left(\frac{y_s}{4}\right)\right], \quad [13]$$

$$Y_2(r_2) = 4e^{\kappa(r_2-a)}\tanh^{-1}\left[e^{-\kappa(r_2-a)}\tanh\left(\frac{y_s}{4}\right)\right], \quad [14]$$

and r_1 and r_2 are the distances from the centers of the first and second spheres, respectively, and are of course related to each other. We calculate the force between the spheres by integrating the Maxwell stress tensor over the median plane between the spheres (1). Clearly, if $Y_1(r_1)$ and $Y_2(r_2)$ are slowly varying compared with other terms in [12] for $r_1 \sim r_2 \sim (a + h/2)$, which is the regime in which contributions to the integral along the median plane for the force are the greatest, Eq. [12] may be well approximated by

$$y(r) \sim Y(h)\left(\frac{a}{r_1}e^{-\kappa(r_1-a)} + \frac{a}{r_2}e^{-\kappa(r_2-a)}\right), \quad [15]$$

for the purpose of evaluating the integral for the force. The function $Y(h)$ is given by

$$Y(h) = 4e^{\kappa h/2}\tanh^{-1}\left[e^{-\kappa h/2}\tanh\left(\frac{y_s}{4}\right)\right]. \quad [16]$$

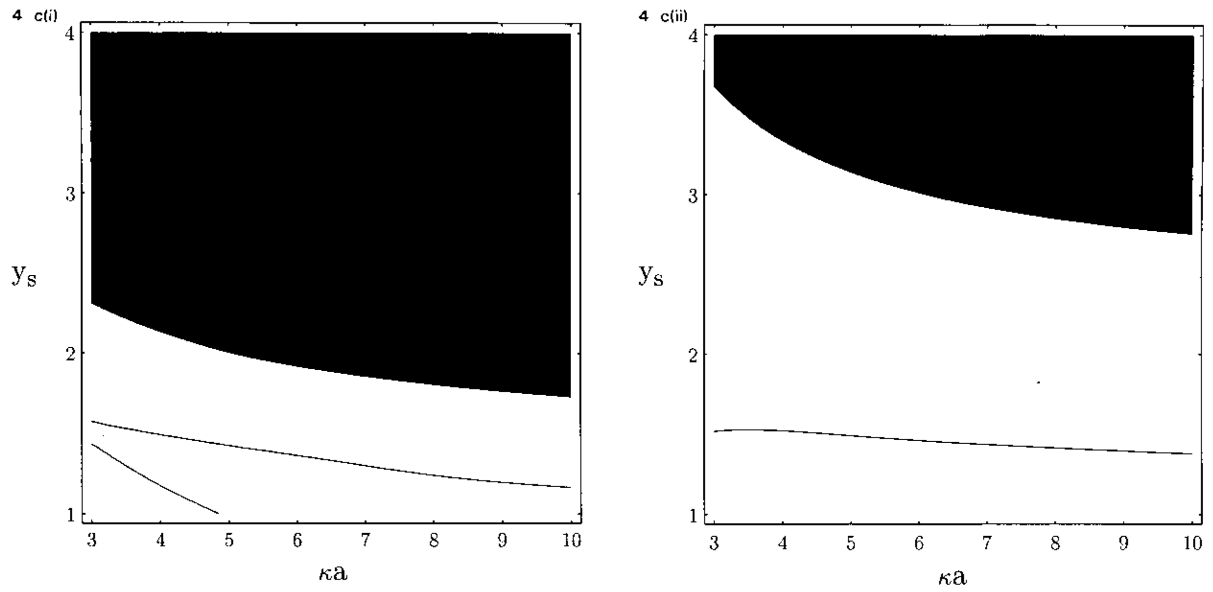

FIG. 4—*Continued*

To illustrate the slowly varying nature of Y with respect to κh for moderate to high potentials, a plot of Y as a function of κh for $y_s \leqslant 4$ is presented in Fig. 2. From the results in Fig. 2 and the form of [15], it is clear that in the evaluation of the force and the interaction free energy, Y may be carried through as a constant to zeroth order.

The analysis then proceeds in a manner analogous to that in (1) and we find the following expressions for the force F and interaction free energy V for two identical spheres:

$$F(h) = \epsilon\left(\frac{kT}{e_0}\right)^2 Y^2(h) a^2 \frac{1+\kappa R}{R^2} e^{-\kappa h}, \qquad [17a]$$

$$V(h) = \epsilon\left(\frac{kT}{e_0}\right)^2 Y^2(h) \frac{a^2}{R} e^{-\kappa h}. \qquad [17b]$$

These are applicable in the regime where the superposition approximation holds. We note that expressions [17] are identical in form to the low-potential (Debye–Huckel) solutions in the superposition approximation limit (1) when the substitution

$$y_s \rightarrow Y(h) \qquad [18]$$

is applied to the low-potential result.

As was discussed by Verwey and Overbeek (10) for the parallel plate case, this suggests that as long as the interaction between the spheres is not very strong, the transformation [18] may be directly applied to the general low-potential solutions for all κh. We thus apply [18] to [8] and to its corresponding expression for the force for the identical sphere case, and obtain the following expressions for the force F and interaction free energy V, valid for all κh, large κa, and up to moderate to high surface potentials ($y_s \leqslant 4$):

$$F(h) = \epsilon\left(\frac{kT}{e_0}\right)^2 Y^2(h) \frac{a^2}{R^2} \times \left\{\ln(1+e^{-\kappa h}) + \kappa R \frac{e^{-\kappa h}}{1+e^{-\kappa h}}\right\}, \qquad [19a]$$

$$V(h) = \epsilon\left(\frac{kT}{e_0}\right)^2 Y^2(h) \frac{a^2}{R} \ln(1+e^{-\kappa h}). \qquad [19b]$$

We note that the expressions for the force and interaction free energy in the superposition limit given in [17] differ from the more familiar expressions (1), i.e., when the function $Y(h)$ is replaced by a constant of proportionality Y_{asym} that characterizes the $e^{-\kappa r}/r$ asymptotic tail of the potential distribution around a single sphere. The constant Y_{asym} is normally found by a numerical solution of the NLPB equation about a single sphere. In the linear Debye–Huckel limit, Y_{asym} is in fact the reduced surface potential y_s. Thus in a heuristic sense, when the surface potential becomes large one can view the function $Y(h)$ as an effective surface potential that varies slowly with separation h.

The results in [19] are the simple formulas we seek in this paper for describing the double-layer interaction between identical particles. These are expected to be accurate up to moderate to high surface potentials ($y_s \leqslant 4$), for modest to large κa values, and for all separations κh, since they are constructed to have the correct asymptotic separation dependence.

We also note that $Y(h)$ was evaluated in the large κa limit, with the κh dependence retained. If, however, $Y(h)$ was evaluated in both the large κa and κh limits, as was performed in (1), then [19] would reduce to

$$F(h) = 16\epsilon\left(\frac{kT}{e_0}\right)^2 \tanh^2\left(\frac{y_s}{4}\right)\frac{a^2}{R^2} \times \left\{\ln(1+e^{-\kappa h}) + \kappa R\frac{e^{-\kappa h}}{1+e^{-\kappa h}}\right\}, \quad [20a]$$

$$V(h) = 16\epsilon\left(\frac{kT}{e_0}\right)^2 \tanh^2\left(\frac{y_s}{4}\right)\frac{a^2}{R}\ln(1+e^{-\kappa h}), \quad [20b]$$

which possess the large κa limiting form for Y_{asym} (1), as expected. Furthermore, as mentioned earlier, at low surface potentials, [19] reduce to the modified HHF formulas [8] for identical spheres.

In the next section we present a quantitative assessment of the key results in Eqs. [8] and [19] by comparison with accurate numerical solutions.

RESULTS

We first consider the accuracy of Eq. [19] for the force and interaction free energy for the double-layer interaction between identical spheres over the parameter space of surface potential y_s and particle size κa. In Fig. 3a, we delineate regions in the κa, y_s domain where the maximum error in [19b] for the interaction free energy is less than 3%, less than 10%, or greater than 10%. The results for sphere separations in the range $0.2 \leq \kappa h \leq 1$ are given in Fig. 3a(i), whereas the results for the range $1 \leq \kappa h \leq 2$ are given in Fig. 3a(ii). In all cases, the benchmark results are obtained from numerical solutions of the NLPB equation at constant surface potential. These results have five-digit numerical accuracy (5). In Figs. 3b(i) and 3b(ii) we present the results of the previous large κa approximate formula [20b] (1). On comparison of Figs. 3a and 3b it becomes clear that [19b] presents a significant improvement over the previous large κa result [20b], while retaining a comparable degree of analytic simplicity. At this stage we should also note that [19b] will clearly approach [20b] as $\kappa h \rightarrow \infty$. Thus as κh is increased we would expect [19b] and [20b] to possess similar accuracies. For completeness, in Figs. 3c(i) and 3c(ii) we present the results for $V(h)$ [19b] when $Y(h)$ has been replaced by Y_{asym}, henceforth referred to as V_{asym}. As discussed previously, Y_{asym} is obtained by a direct numerical solution of the NLPB equation for a single sphere. Although V_{asym} is no longer analytic in form, as it requires a numerical solution of the NLPB equation and this is out of the scope of the present paper, it has been presented since it is the most accurate previous result attainable via the Verwey and Overbeek (10)-type extension of the low-potential results to the high-potential regime (1). As is clear from Figs. 3a(i), 3b(i), and 3c(i), [19b] represents an improvement not only on [20b] but also on V_{asym} for the range $0.2 \leq \kappa h \leq 1$. This is a result of the fact that the κh dependence has been retained in the derivation of $Y(h)$, whereas the limit $\kappa h \rightarrow \infty$ has been taken in the evaluation of Y_{asym} (1). This is an excellent result when it is noted that [19b] is in fact entirely a large κa result, whereas V_{asym} has an obvious κa dependence from

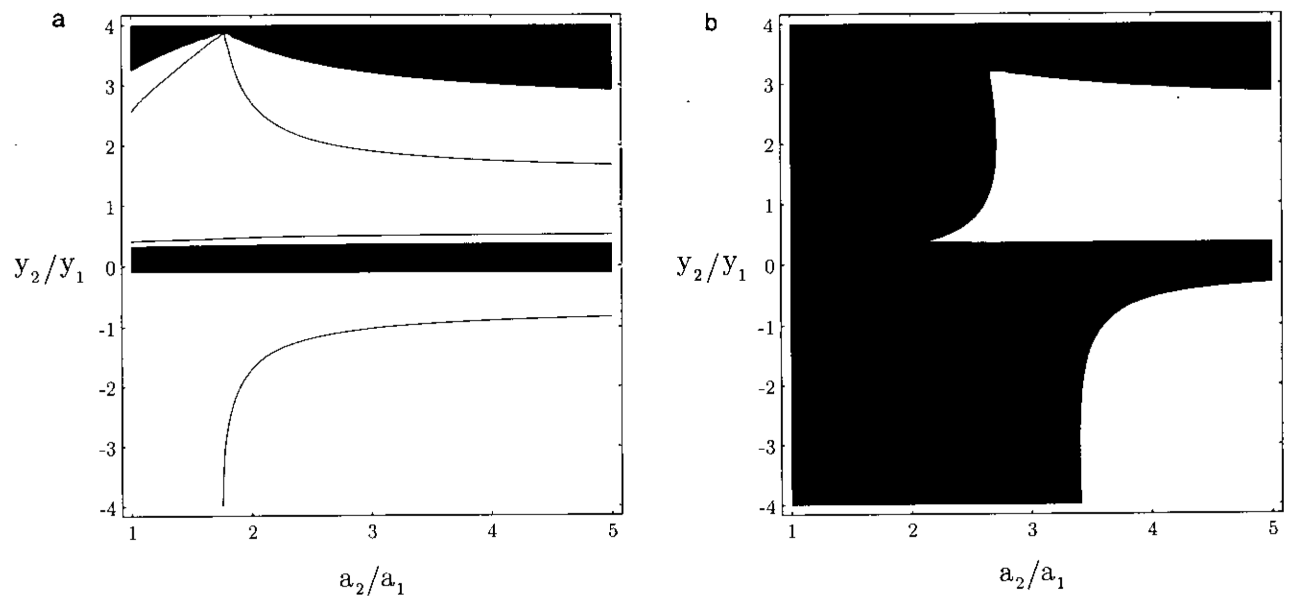

FIG. 5. Magnitude of the maximum relative error of the low-potential interaction free energy $V(h)$ between dissimilar spheres, in the surface potential ratio (y_2/y_1) and radius ratio (a_2/a_1) domain, for $\kappa a_1 = 5$ and $0.2 \leq \kappa h \leq 2$. (a) Modified HHF; (b) HHF. In the white region the error is less than 3%, in the gray region, less than 10%; and in the black region, greater than 10%.

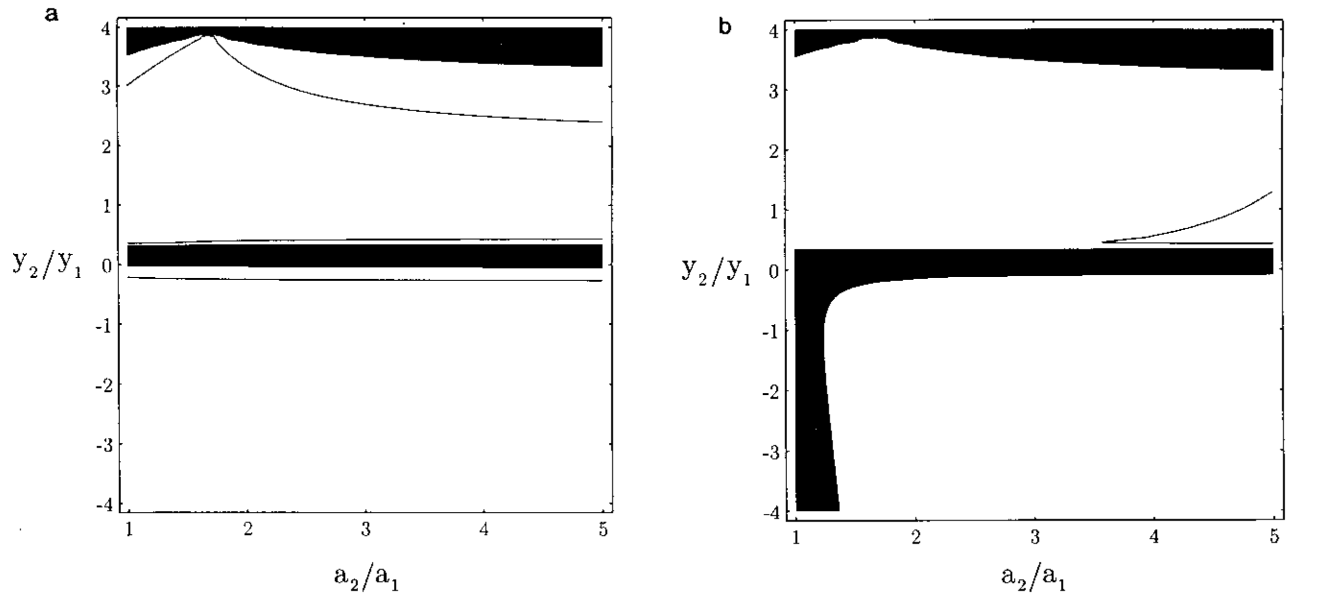

FIG. 6. As for Fig. 5 with $\kappa a_1 = 10$.

Y_{asym}. We then consider Figs. 3a(ii), 3b(ii), and 3c(ii), where we see that although [19b] gives greater accuracy than [20b], it gives less accuracy than V_{asym} for the range $1 \leqslant \kappa h \leqslant 2$. To explain this we note that as $\kappa h \to \infty$, V_{asym} will give the exact result for all κa (1), whereas [19b] is strictly speaking a large κa result. Thus it is not surprising that as κh is increased, V_{asym} gives greater accuracy than [19b]. However, we must point out that both [19b] and V_{asym} gave very good results, with errors less than 10% in the entire domains of Figs. 3a(ii) and 3c(ii).

In Fig. 4 we present a similar comparison for the force between two identical spheres [19a], the previous large κa formula [20a] and F_{asym} (which is defined analogously to V_{asym} above). As for the interaction free energy, we again observe that the new [19a] presents a significant improvement over the previous large κa result [20a], for the region $0.2 \leqslant \kappa h \leqslant 1$. In this case, however, [19a] also gives greater accuracy than F_{asym} for the entire range $1 \leqslant \kappa h \leqslant 2$. It should again be noted that as $\kappa h \to \infty$, F_{asym} is exact for all κa.

We now consider the accuracy of the modified HHF formula [8] for the interaction free energy at constant potential between dissimilar spheres in the Debye–Huckel treatment. In this case our parameter domain is the ratio of surface potentials (y_2/y_1) and the ratio of sphere radii (a_2/a_1). The benchmark results for this comparison are obtained from numerical eigenfunction expansion solutions of [1], which are accurate to five significant figures (4). As before we delineate regions in the domain a_2/a_1, y_2/y_1, where the maximum error is less than 3%, less than 10%, and greater than 10%. In Fig. 5a we show such results for $\kappa a_1 = 5$ and $0.2 \leqslant \kappa h \leqslant 2$ for the modified HHF formula [8] and in Fig. 5b the corresponding results for the HHF result. The superiority of the modified HHF formula is self-evident. The region of high error in Fig. 5a along $y_2/y_1 = 0$ arises from the combinations of the facts that when y_2/y_1 is small in magnitude (i) the interaction free energy changes sign in the κh region under consideration, so the relative error becomes deceivingly large, and (ii) the interaction free energy is also small, resulting in a magnification of the relative error. In Fig. 6, we present a similar comparison for $\kappa a_1 = 10$, and the accuracies of the modified HHF and HHF formulas improve as expected at the larger value of κa_1. We should also note that the modified HHF formula gives accuracy comparable to that of the Bell *et al.* (1) result; however, its analytic simplicity is similar to that of the original HHF formula, and thus it is much simpler than the original Bell *et al.* (1) result. Furthermore, as $\kappa h \to 0$, the modified HHF result approaches the HHF result, as does the formula of Bell *et al.* (1).

CONCLUSION

We have presented simple analytic formulas for the interaction between two colloidal particles, at constant surface potential. This involved reanalysis of the formulation of Bell *et al.* (1) under a simplified but equivalent set of approximations. From this we showed that under the Debye–Huckel treatment, the original HHF formula, which is valid only for small κh, may be trivially modified to obtain the modified HHF result and thus extend its region of validity to all κh.

We then presented the extension of the modified HHF result to the moderate- to high-potential regime, for the case of two identical spheres. This extension maintains analytic simplicity similar to that of the previous large κa formulation, but is significantly more accurate. We also compared its accuracy against the semianalytic result when $Y(h)$ is replaced by Y_{asym} (which is evaluated numerically), and demonstrated that in general greater accuracy is attained by the present formulas, for the regime $\kappa h \sim 1$.

It is thus recommended that these new formulas should be used in place of the familiar HHF result and its previous extension to the high-potential regime (1).

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