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Upper-bound Error Estimates for the Derjaguin Approximation and the Linearization Approximation to the Double-layer Interaction Energy for Two Unequal Spheres

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At present only approximate methods are available for calculating double-layer interaction energy. All of these approximate methods use the Derjaguin approximation, which is valid for large 'plate-like' spheres. When the linearization approximation is used in addition to the Derjaguin approximation, further computational simplification results in an analytic expression for the double-layer interaction energy. This linearization approximation is valid for small surface potentials. This work estimates the upper-bound error in the double-layer interaction energy caused by the Derjaguin approximation and the linearization approximation. These error estimates are shown to be a function of the sphere radius and surface potential.

The double-layer interaction energy of two unequal spheres is an important problem of colloid science because it is fundamental to coagulation and particle adhesion.[1,2] The double-layer interaction energy for two unequal spheres is approximated with the Derjaguin approximation[3,4] or both the Derjaguin approximation and the linearization approximation.[5] The Derjaguin approximation decomposes the interacting edges of the two spheres into a series of flat rings. For each pair of interacting flat rings, the parallel-plate solution to the Poisson–Boltzmann (PB) equation is used to calculate the double-layer interaction energy. The linearization approximation uses the linearized PB equation instead of the non-linear PB equation for calculation of the double-layer interaction energy. The Derjaguin approximation is valid for large 'plate-like' spheres where the dimensionless radius is greater than five. The linearization approximation is valid for small surface potentials where the dimensionless surface potential is less than one. This work estimates the upper-bound error in the double-layer interaction energy caused by the Derjaguin approximation and the linearization approximation. Error estimates for both these approximations are plotted against the dimensionless radius and dimensionless surface potential.

FORMULATION

To estimate the error in the double-layer interaction energy for two unequal spheres caused by the Derjaguin approximation and the linearization approximation, it is useful to analyse the problem of a single sphere in a z–z electrolyte solution. The dimensionless potential, Ψ, in the electrolyte solution surrounding the sphere is given by the PB equation:

$$\nabla^2\Psi = \sinh \Psi. \tag{1}$$

In spherical coordinates the Laplacian operator is given by

$$\nabla^2\Psi = \frac{\partial^2\Psi}{\partial R^2} + \frac{2}{R}\frac{\partial\Psi}{\partial R} \tag{2}$$

where R is the dimensionless radius κr and κ is the Debye-Hückel parameter. Constant-potential boundary conditions are used such that $\Psi = \Psi_0$ at the surface of the sphere, or $R = A$. The electrostatic energy, E, of the charge distribution surrounding the single sphere is given explicitly by

$$E = \frac{1}{2}\int_{\bar{A}} \sigma_0\Psi_0 \frac{kT}{zq}\,\mathrm{d}\bar{A} \tag{3}$$

where σ_0 is the surface charge density defined by

$$\sigma_0 = \frac{-\varepsilon}{\kappa}\frac{kT}{zq}\frac{\mathrm{d}\Psi}{\mathrm{d}R}\bigg|_{R=A} \tag{4}$$

where ε is the permittivity of the medium, k is Boltzmann's constant, T is the absolute temperature and q is the fundamental charge. In spherical coordinates the infinitesimal area, $\mathrm{d}\bar{A}$, is given by

$$\mathrm{d}\bar{A} = \frac{R^2}{\kappa^2}\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi. \tag{5}$$

The expression for the electrostatic energy, eqn (3), can be integrated to give

$$E = \frac{-2\pi\varepsilon A^2}{\kappa}\left(\frac{kT}{zq}\right)^2\Psi_0\frac{\partial\Psi}{\partial R}\bigg|_{R=A}. \tag{6}$$

As such, the electrostatic energy is the energy required to generate the potential distribution of the double layer.

To use this methodology to calculate the double-layer interaction energy for two unequal spheres, we must solve the PB equation in bispherical coordinates and calculate the electrostatic energy for both spheres.[6] In this case the electrostatic energy for each sphere becomes a function of the separation between spheres, S [*i.e.* $E(S)$]. The double-layer interaction energy, $\Delta E(S)$, for the two unequal spheres (1 and 2) is given by[6-8]

$$\Delta E(S) = [E_1(\infty) + E_2(\infty)] - [E_1(S) + E_2(S)]. \tag{7}$$

This method of calculating the double-layer interaction energy has not so far been possible because the solution to the PB equation in bispherical coordinates is not available, necessitating approximations. The error in the double-layer interaction energy incurred by these approximations results from errors in each of two terms, $[E_1(\infty) + E_2(\infty)]$ and $[E_1(S) + E_2(S)]$. Because these two terms are subtracted, errors in the second term are subtracted from errors in the first term. In the case of $\Delta E(\infty)$ the errors in the two terms cancel. For other separations the errors in each of the two terms will not completely cancel. This work evaluates the error in the $[E_1(\infty) + E_2(\infty)]$ term caused by approximation. The error in this term is an upper-bound estimate of the error in the double-layer interaction energy for two unequal spheres.

Using the above formulation for the Laplacian operator in spherical coordinates, eqn (2), the Derjaguin approximation assumes that the second term, $(2/R)\,\partial\Psi/\partial R$, is negligible compared with the first term, $\partial^2\Psi/\partial R^2$. This approximation is equivalent to the one-dimensional or flat-plate Laplacian and neglects the curvature of the

spherical surface. The linearization approximation assumes that the right-hand side of eqn (1), sinh Ψ, can be linearized to Ψ. This approximation is valid for small values of Ψ.

RESULTS

The exact solution to the linearized PB equation in spherical coordinates gives the following slope to the potential distribution:

$$\frac{\partial \Psi}{\partial R} = \frac{-\Psi_0 A}{R} \exp(A - R)\left(\frac{1}{R} + 1\right). \tag{8}$$

The electrostatic energy for the sphere using this slope for the potential distribution is

$$E_{\mathrm{LA}} = \frac{2\pi\varepsilon}{\kappa}\left(\frac{kT}{zq}\right)^2 \Psi_0^2 A(1 + A). \tag{9}$$

The exact solution to the one-dimensional linearized PB equation gives the following slope to the potential distribution:

$$\frac{\partial \Psi}{\partial R} = -\Psi_0 \exp(A - R). \tag{10}$$

The electrostatic energy of the sphere using this slope for the potential distribution is

$$E_{\mathrm{DA,LA}} = \frac{2\pi\varepsilon}{\kappa}\left(\frac{kT}{zq}\right)^2 \Psi_0^2 A^2. \tag{11}$$

The exact solution to the one-dimensional non-linear PB equation gives the following slope to the potential distribution:

$$\frac{\partial \Psi}{\partial R} = (2\cosh \Psi - 2.0)^{1/2}. \tag{12}$$

The electrostatic energy of the sphere using this slope for the potential distribution is

$$E_{\mathrm{DA}} = \frac{-2\pi\varepsilon}{\kappa}\left(\frac{kT}{zq}\right)^2 \Psi_0 A^2 (2\cosh \Psi_0 - 2.0)^{1/2}. \tag{13}$$

The subscripts on the electrostatic energies in eqn (9), (11) and (13) correspond to the approximations used in the calculation (*i.e.* DA Derjaguin approximation and LA linearization approximation).

A comparison of $E_{\mathrm{DA,LA}}$ with E_{LA} shows the error caused by the Derjaguin approximation for small surface potentials. The ratio of $E_{\mathrm{DA,LA}}$ to E_{LA} is plotted in fig. 1 against the radius. This plot shows that the Derjaguin approximation underestimates the energy for all radii. At large radii the Derjaguin approximation gives relatively accurate values of the energy. But as the radius decreases, the error caused by the Derjaguin approximation gets progressively larger. For example, at a radius of 5, the error is 17%, at a radius of 1, the error is 50% and at a radius of 0·5, the error is 66%.

A comparison of $E_{\mathrm{DA,LA}}$ with E_{DA} shows the error caused by the linearization approximation for large plate-like spheres. The ratio of $E_{\mathrm{DA,LA}}$ to E_{DA} is plotted

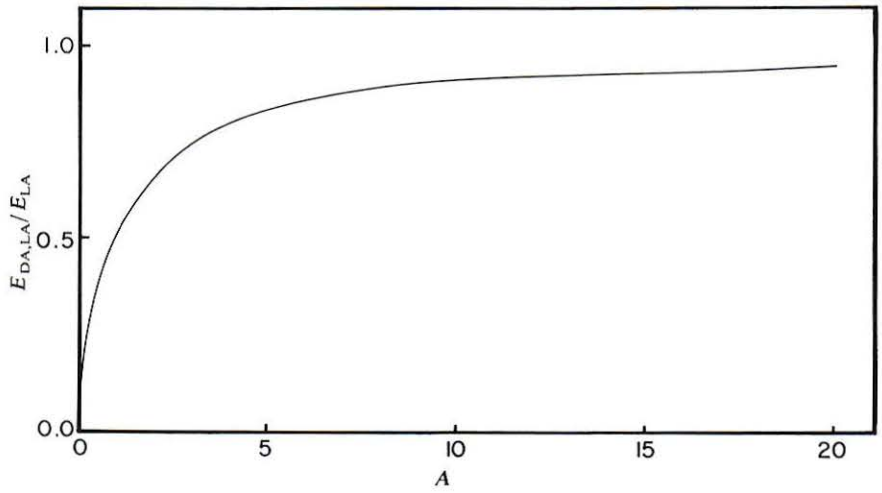

Fig. 1. Error caused by the Derjaguin approximation for small surface potentials.

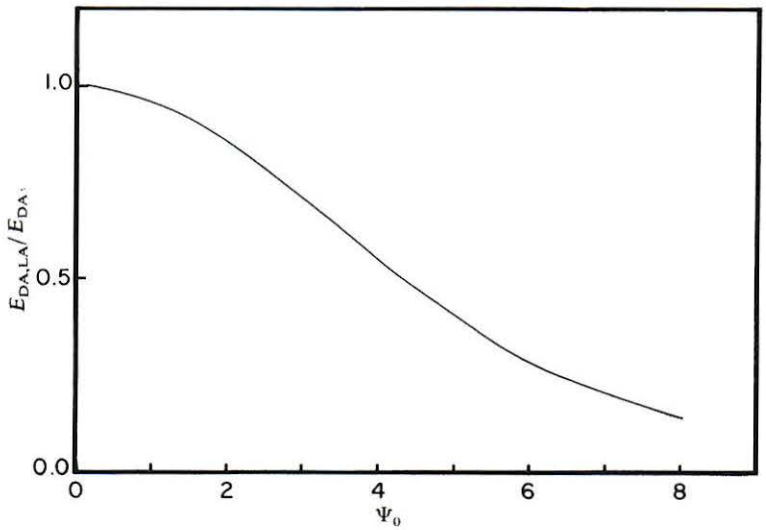

Fig. 2. Error caused by the linearization approximation for large radius spheres.

in fig. 2 against the surface potential. This plot shows that the linearization approximation also underestimates the energy for all potentials. At small values of potential, the linearization approximation gives accurate values of the energy, but as the potential increases the error increases. For example, at a potential of 2, the error is 14%, at a potential of 4, the error is 44% and at a potential of 8, the error is 85%.

To obtain the error in the energy caused by the Derjaguin approximation for large surface potentials as well as the error in the energy caused by the linearization approximation for small radii, we need the exact solution to the two-dimensional non-linear PB equation, which at present is unavailable. However, a numerical solution has been obtained by Loeb *et al.*[9] Tabulated values of $\partial\Psi/\partial R|_{R=A}$ were

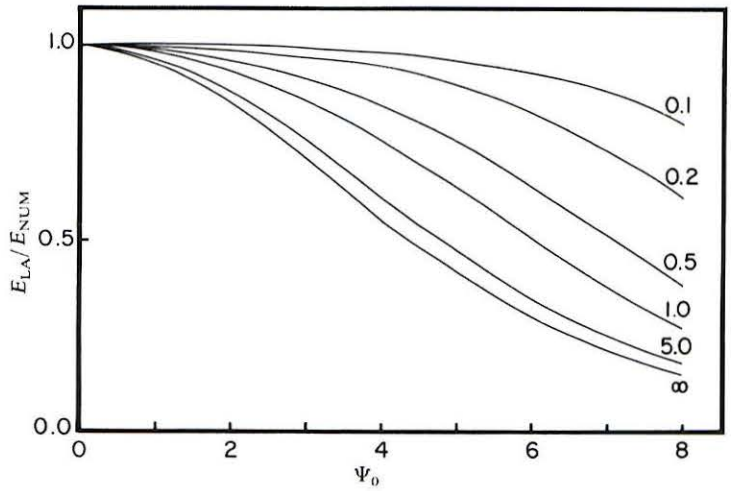

Fig. 3. Error caused by the linearization approximation; values of A are shown on the curves.

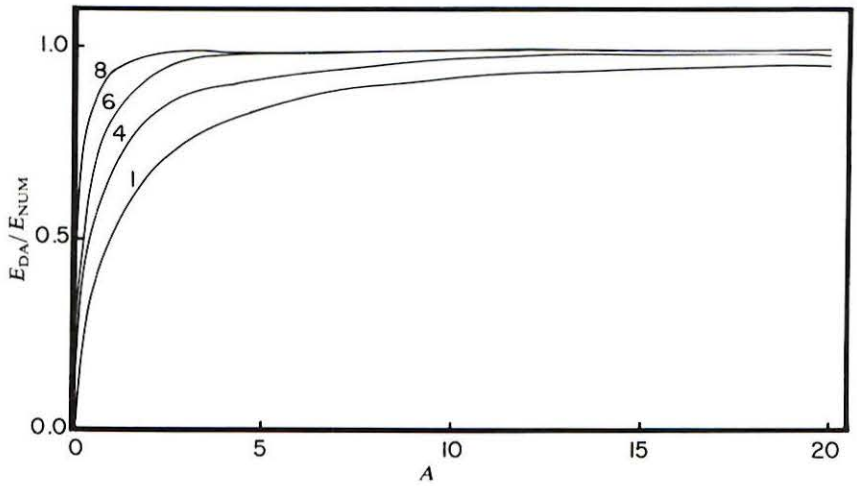

Fig. 4. Error caused by the Derjaguin approximation; values of Ψ_0 are shown on the curves.

used to evaluate the electrostatic energy, E_{NUM}, for a sphere with any radius and any surface potential.

Using this numerical solution, the error in the energy caused by the linearization approximation is shown in fig. 3, where the ratio of E_{LA} to E_{NUM} is plotted against Ψ_0 for various values of radius. For $A \to \infty$, fig. 2 is reproduced. At smaller values of the radius the error in the energy is decreased for all potentials.

The error in the energy caused by the Derjaguin approximation is shown in fig. 4, where the ratio of E_{DA} to E_{NUM} is plotted against the radius for various values of potential. For $\Psi_0 \to 0$, fig. 1 is reproduced. At larger values of potential, the error in the energy caused by the Derjaguin approximation decreases. At a radius of 2, the error at a potential of 1 is 31%, while at a potential of 8 the error is only 4%.

Table 1. 90% accuracy conditions

A	Ψ_0
linearization approximation	
∞	<1.5
5	<1.75
1	<2.5
0.2	<5
0.1	<6.5
Derjaguin approximation	
>9	$\rightarrow 0$
>4	4
>1.5	6
>0.5	8
both Derjaguin and linearization approximations	
∞	<1.5
20	<1.3
10	<0.5
<5	not possible

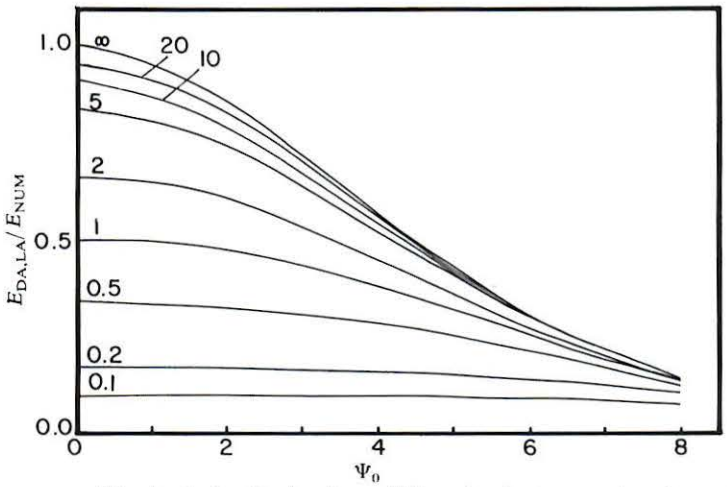

Fig. 5. Error caused by both the Derjaguin and linearization approximations; values of A are shown on the curves.

The error in the energy caused by both the Derjaguin approximation and the linearization approximation is shown in fig. 5, where the ratio of $E_{DA,LA}$ to E_{NUM} is plotted against the surface potential for various values of radius. For $A \rightarrow \infty$, fig. 2 is reproduced. For smaller radii, the error in the energy increases for all values of potential. The amount of the error increase is dependent upon both the radius and the potential.

CONCLUSIONS

The approximate methods discussed in this work underestimate the electrostatic energy for a single sphere. The values of radius and potential for which the various approximations give > 90% accuracy are shown in table 1. Note that energy values calculated with both the Derjaguin and linearization approximations are <90% accurate when the radius is <5, no matter what potential is used.

The utility of these calculations can be observed by considering the interaction of two unequal spheres at a separation of $S = 1$ in a 1:1 electrolyte solution with $\kappa = 10^9\ m^{-1}$: for sphere 1, $A = 5$ and $\Psi_0 = 5$; for sphere 2, $A = 10$ and $\Psi_0 = 3$. The double-layer interaction energy is $21kT$ using the expression of Hogg *et al.*[5] This expression uses both the Derjaguin approximation and the linearization approximation. An upper-bound estimate of the error caused by these two approximations can be obtained from fig. 5. The error resulting from $E_1(\infty)$ is 58%, while that resulting from $E_2(\infty)$ is 33% for a weighted average error of 43%. This 43% is an estimate of the largest possible error in the $21kT$ calculated from ref. (5).

One of the referees of ref. (6) is thanked for elucidating the problem addressed in this work.

NOMENCLATURE

A	dimensionless sphere radius
$\bar{A}$	surface area
E	electrostatic energy of a single sphere
$E_1(S)$, $E_2(S)$	electrostatic energy of spheres 1 and 2 separated by a distance S
$\Delta E(S)$	double-layer interaction energy for two unequal spheres at a distance S
E_{LA}	electrostatic energy calculated with the linearization approximation
E_{DA}	electrostatic energy calculated with the Derjaguin approximation
E_{NUM}	electrostatic energy calculated with the numerical solution to the PB equation
k	Boltzmann's constant
q	fundamental charge
r	radial coordinate
R	dimensionless radial coordinate
S	dimensionless separation
T	absolute temperature
z	valence of the electrolyte
ε	permittivity of the medium
θ	angular coordinate
κ	Debye-Hückel parameter
σ_0	surface charge density
ϕ	azimuthal coordinate
$\Psi_{(0)}$	dimensionless potential (surface)

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