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ORIGINAL CONTRIBUTION

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Approximate expressions of determining the double layer energy and force of interaction between two charged colloidal spheres

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Abstract The approximate expressions have been obtained to calculate the electrical double layer energy and force between two spherical colloidal particles based on the improved Derjaguin approximation. Results for identical spheres interacting under constant surface potential, constant surface charge are given. Comparison of present results with numerical results calculated by Carnie and Chan is made. The expressions are found to work quite well for the constant surface potential case, and for the constant charge case, we make correction for the expressions. The results given are satisfactory provided $\kappa h \geq 0.4$.

Key words Force – energy – sphere – Derjaguin method

In the DLVO theory, the electrical double layer interaction is based on the nonlinear Poisson–Boltzmann theory. However, in spite of the relative simplicity of Poisson–Boltzmann theory for the electrostatic potential, the equation can only be solved in closed form in the planar geometry. For interaction between spheres or curved surfaces, one must resort to some form of approximation. In 1956, Hoskin and Levine [1] made the first attempt to obtain numerical solutions of the linear Poisson–Boltzmann equation for identical spheres interacting under constant surface potential. McCarthey and Levine [2] returned to the same problem using the finite difference approach and a large mesh size (30×40).

Owing to the limitations then, at that time computational power of the computer was poor. With the advent and the spread of modern high speed computers, such calculations once again come into use. Glendinning and Russell [3] solved the linearized equation using a multipole expansion to compute the force between two identical charged spheres for the constant potential and the constant charge conditions. Later, Carnie and Chan et al. [4, 5] extended theses results to include the cases of nonlinear equation, again considering identical double layers. Numerical results of interaction energy for unequal spherical double layers were obtained by Palker and Lenhoff [6].

The calculation of numerical results has become easy with the help of modern high speed computers. However, numerical solution of PB equation is a very difficult computational problem, one requires specialized skill, but colloid chemists are not necessary to possess this skill. The

aim of the numerical solution is to provide a quantitative statement regarding the applicability of various approximate expressions and to provide information regarding the circumstance under which each common approximate theory can be used and the error that would be incurred. Therefore, various approximate theories, specially, both the linear superposition approximation [7] and Derjaguin's method [8] are most in use in the literature. The utility of the two methods is totally different, or the exact opposite, linear superposition approximation is capable of calculating interaction for small κa and large κh, and Derjaguin method for large κa and small κh (where a is the sphere radius, h is distance of closest approach between the sphere radii, $1/\kappa$ is the Debye screening length of the electrolyte). References [4, 5] are desirable to visualize the accuracy of each approximate method for different combination of scaled sphere radius, κa, and scaled distance, κh, and indicated in the parameter space of (κa, κh) regions for which the magnitude of the error of each approximation is less than 10%.

In previous work we have proposed an improved Derjaguin approximation (IDA) [9] which made a simple curvature correction and nearly extended the applicability of Derjaguin approximation to all regions in (κa, κh) parameter space for interaction free energy at constant surface potential condition between two identical spheres, provided surface potential is low. In this paper we shall show that IDA can be applied also to the case of constant surface charge and the computation of force between spherical colloidal particles.

According to IDA, the equation for interaction energy between two spheres with equal radius a can read [9]

$$V_R = \pi a \int_h^\infty V(h)\left(1 - \frac{\kappa h}{2\kappa a} + \frac{1}{2\kappa a}\right) dh\,, \tag{1}$$

where $V(h)$ is the interaction free energy per unit area between interacting parallel plates, can be found by solving the one-dimensional Poisson–Boltzmann equation.

We consider particles which maintain a uniform fixed surface potential during interaction $\sim$ the constant potential model.

$$V_R = 4\pi\varepsilon_o\varepsilon_r a\psi^2\left(\frac{a}{R}\right)\ln(1 + e^{-\kappa h})\,. \tag{2}$$

Here, ε_r is the dielective constant of the solution and ε_o is the permittivity of free space, while ψ is the surface potential, $R = 2a + h$.

Interaction force at the constant potential model is

$$F_R = 4\pi\varepsilon_o\varepsilon_r\psi^2\left(\frac{a}{R}\right)^2\left[\ln(1 + e^{-\kappa h}) + \frac{\kappa R e^{-\kappa h}}{1 + e^{-\kappa h}}\right]. \tag{3}$$

During interaction particles maintain a uniform fixed surface charge density $\sim$ the constant charge model

$$V_R^\sigma = -4\pi\varepsilon_o\varepsilon_r\psi^2\left(\frac{a}{R}\right)\ln(1 - e^{-\kappa h})\,. \tag{4}$$

Interaction force at the constant charge model is

$$F_R^\sigma = 4\pi\varepsilon_o\varepsilon_r\psi^2\left(\frac{a}{R}\right)^2\left[-\ln(1 - e^{-\kappa h}) + \frac{\kappa R e^{-\kappa h}}{1 - e^{-\kappa h}}\right]. \tag{5}$$

Generally speaking, Eqs. (2)–(5) give the correct behavior at low potential because at Eq. (1) $V(h)$ used to integrate can be applied only to the case of low surface potential. Within improved Derjaguin approximation, no restrictions are imposed upon the magnitude of the surface potential. However, when the surface potential is high, the nonlinearity of PB equation will also cause the potential to fall rapidly away from the particles surface, and we would there expect the accuracy of the IDA to ensure as the surface potential increase.

In order to assess the validity of the analytic expression given here for the interaction free energy and the force we will take the linearized PB theory as the basis, which provides a fairly accurate qualitative and quantitative description of the system as long as the surface potential of the particles is less than or comparable to the thermal potential (kT/e) (where k is the Boltzmann constant, T is absolute temperature, while e is elementary charge).

Here, we define the relative error as

$$E\% = \left(\frac{\text{Approximate} - \text{Exact}}{\text{Exact}}\right) \times 100\% \tag{6}$$

for various values of κa and κh. For Eq. (2) it is unnecessary to go into details because it had been discussed in the previous work [9]. In Fig. 1 we display the error % of the force via Eq. (3) under constant potential as a function of particle separation for κa in the range 0.5 to 10. Upper and lower limit of error% is $\pm$ 10%, in the region we can recommend the use of approximate expressions. When $\kappa a \geq 0.5$, $\kappa h \geq 0.4$ Eq. (3) is good approximation with relative errors less than $\pm$ 10%. As the magnitude of κa increases the region of accuracy in the (κa, κh) domain increases. If $\kappa h > 3$ the relative errors are less than 3% for all values of κa. When $\kappa a \geq 10$ maximum relative error are less than 5% for all values of κh.

For interaction under constant charge, the error in the classical Derjaguin formula is unacceptably large for all combinations of κa and κh, except when $\kappa a > 10$. Equation (4) and (5) decrease the magnitude of the error to a certain extent. They are accurate for $\kappa h \geq 2$, but as κh goes to zero the error is unacceptably large. Derjaguin formulas, and Eq. (4) or Eq. (5) go to infinite if $\kappa h \to 0$. This is because at constant charge the energy and the force

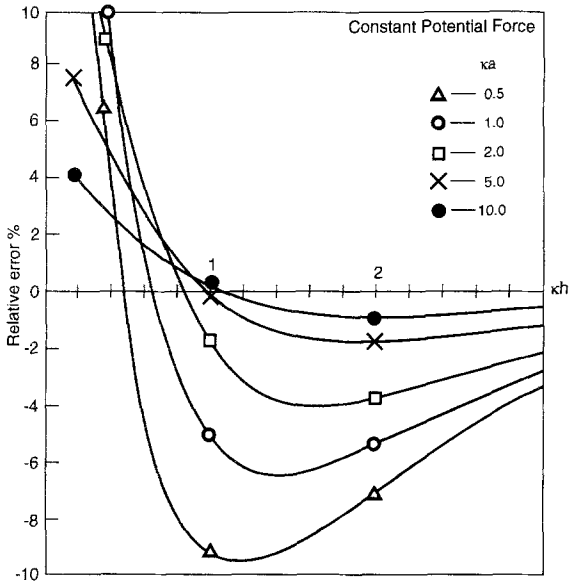

Fig. 1 The magnitude of the relative error of the interaction force according to Eq. (3) for $\kappa a = 0.5\,(\triangle)$, $1.0\,(\circ)$, $2.0\,(\square)$, $5.0\,(\times)$ and $10\,(\bullet)$ at constant surface potential. Exact values are calculated by Carnie and Chan's method

between identical spheres remain finite as separation goes to zero. However, as separation goes to zero, the interaction free energy per unit area at constant charge between plates diverges, Therefore, at small separation Derjaguin approximation, and thus IDA must again overestimate the energy and force. Further, for both constant potential and constant charge, the linearized theory gives accurate results as long as the surface potential is not much higher than kT/e. However, for constant charge density interaction, the surface potential start increasing as two spheres approach each other. Hence, at large gap distance the linearized theory works well, and it starts deviating after the surface potential exceeds 1 kT/e. As with the above Eq. (4) and Eq. (5) are poor for small κh. In order to achieve better results Eq. (4) can be expanded in a power series of $e^{-\kappa h}$, and the first two terms only are taken:

$$V_R^\sigma = 4\pi\varepsilon_0\varepsilon_r a\left(\frac{a}{R}\right)\left(e^{-\kappa h} + \frac{1}{2}e^{-2\kappa h}\right). \tag{7}$$

Relevant force is

$$F_R^\sigma = 4\pi\varepsilon_0\varepsilon_r\psi^2\left(\frac{a}{R}\right)^2\left[\left(e^{-\kappa h} + \frac{1}{2}e^{-2\kappa h}\right) + \kappa R\cdot(e^{-\kappa h} + e^{-2\kappa h})\right] \tag{8}$$

Equations (7) and (8) are identical to Eqs. (4) and (5) at large gap distance. It is to be noted that Eqs. (4) and (5) go to infinite if $\kappa h \to 0$, but Eqs. (7) and (8) remain finite if $\kappa h \to 0$. However, in the case of $\kappa a < 2$ their relative error goes beyond the limit of 10% except when $\kappa h > 1.5$ for energy; $\kappa h > 2$ for force. The approximate values of Eqs. (7) and (8) are always larger than the exact values. As the magnitude of κa increases the approximate values can be larger or smaller than the exact values. We therefore introduce a trial term into the expression of the force and its integrated form in conformity with the method suggested by Honig and Mul [10], such that

$$F_R^\sigma = 4\pi\varepsilon_0\varepsilon_r\psi^2\left(\frac{a}{R}\right)^2\left[-\ln(1-e^{-\kappa h}) + \kappa R\cdot(e^{-\kappa h} + e^{-2\kappa h}) - \frac{1}{2}(3+\kappa h)e^{-2\kappa h}\right] \tag{9}$$

and

$$\begin{aligned} V_R^\sigma &= 4\pi\varepsilon_0\varepsilon_r a\psi^2\left(\frac{a}{R}\right)\left\{\left(e^{-\kappa h} + \frac{1}{2}e^{-2\kappa h}\right) - \frac{1}{2}e^{-2\kappa h}\left[3 - \frac{3R}{R+h} + \frac{\kappa R(1+2\kappa h)}{4(\kappa R + 5\kappa h)^2}\right]\right\} \\ &= \text{Eq. (7)} - 2\pi\varepsilon_0\varepsilon_r a\psi^2\left(\frac{a}{R}\right)\cdot e^{-2\kappa h}\cdot\left[3 - \frac{3R}{R+h} + \frac{\kappa R(1+2\kappa h)}{4(\kappa R+5\kappa h)^2}\right] \end{aligned} \tag{10}$$

or

$$V_R^\sigma = \text{Eq. (7)} - 2\pi\varepsilon_0\varepsilon_r a\psi^2\left(\frac{a}{R}\right)\cdot e^{-2\kappa h}\left(3 - \frac{3R}{R+h} + \frac{1}{2}\kappa h e^{-3\kappa h}\right) \tag{10A}$$

It is noted that the integration of Eq. (9) does not constitute an exact solution. We resort to integral intermediate value theorem and trial and error to obtain Eq. (10) or Eq. (10A), which are different in approach but equally satisfactory in result.

In Figs. 2 and 3, we examine the accuracy of interaction energy and force calculated according to Eqs. (9) and Eq. (10) under the constant charge model. Fig. 2. energy, Fig. 3; force. In Fig. 2, we see that the error in the energy of constant charge is less than 1% for $\kappa h \geq 2$; and 2% for $\kappa h \geq 1$ in the range $0.5 \leq \kappa a \leq 10$. When $\kappa h < 1$ relative error increases but if $\kappa h \geq 0.2$ the error% is still less than $\pm$ 10% except the individual points, for example, when $\kappa a \geq 5$ at $\kappa h = 0.2$. However, even if $\kappa a = 10$ at $\kappa h = 0.2$ relative error is about $-$ 19%. If no great precision is required as long as $\kappa h \geq 0.2$ Eq. (10) can be used.

In the case of $\kappa a > 10$ results underestimated for the energy at smaller separations will be unsatisfactory. In this

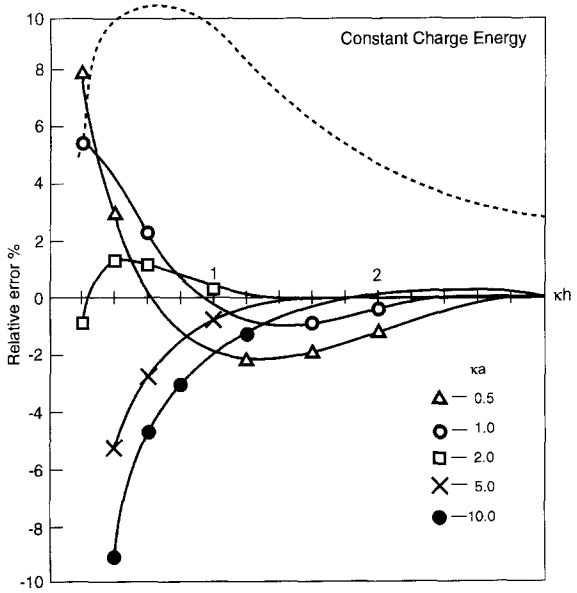

Fig. 2 The magnitude of relative error of the interaction free energy according to Eq. (10) at constant surface charge. The dotted line indicates the relative error of Eq. (7) for $\kappa a = 2$. Other as for Fig. 1

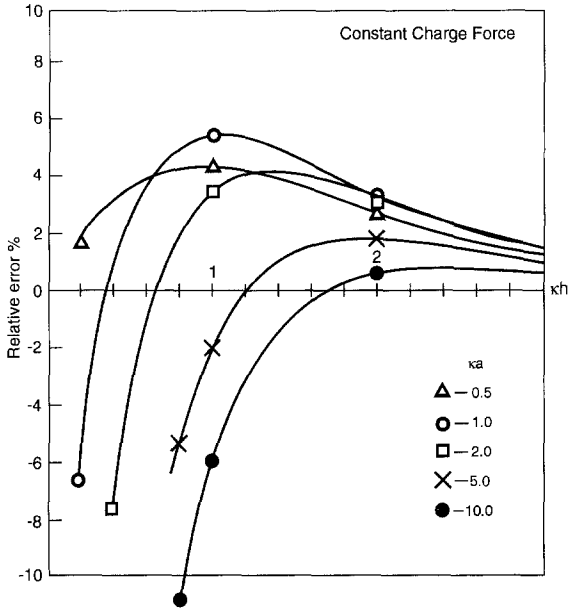

Fig. 3 As for Fig. 1, but comparing Eq. (9) at constant surface charge

case, we suggest that Eq. (10) can change into the difference between Eq. (4) and correct term.

In Fig. 2 we show the relative error of Eq. (7) for $\kappa a = 2$ (dotted line). Equation (10) shows a marked decrease of the relative error; maximum relative error is decreased from 10.6% to 1%.

Figure 3 is the relative error of the force obtained via Eq. (9) under constant charge model. Results are given for five values of κa: $\kappa a = 0.5, 1, 2, 5$ and 10. Results overestimate the force at large separations but fall below the exact results at smaller separations. For $\kappa h > 3$ error% is less than 1%, and less than 3.5% for $\kappa h \geq 2$. In the range $1 \leqslant \kappa h \leqslant 2$ maximum relative error is about -6.0% ($\kappa a = 10$). In the range $0.5 \leq \kappa a \leq 1$ as long as $\kappa h \geq 0.2$ Eq. (9) is accurate to within $\pm$ 10%, but for larger κa 10% boundary moves toward larger κh value.

We have derived explicit formulas for the interaction energy and force between two spheres under both constant potential and constant charge model according to improved Derjaguin approximation. Under constant charge model the results given are not as good as constant potential model. The IDA is less accurate in predicting the force than the interaction free energy. For this reason we make correction for expressions of constant charge to obtain Eqs. (9) and (10). They give asymptotical behavior at large separation, when $\kappa h \geq 1$ the results are in good agreement with the exact numerical results of Carnie and Chan [4]. If $\kappa h < 1$ results are also satisfactory provided $\kappa h \geq 0.4$.

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