Diffuse double layer interaction between two spherical particles with constant surface charge density in an electrolyte solution

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With 2 figures

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I. Introduction

Recently, the diffuse double layer interaction between two spherical particles with constant surface charge density in an electrolyte solution was calculated by several investigators (1–5) on the basis of Derjaguin's method (6), which makes it possible to calculate the interaction of spheres from that of plates. However, the influence of the electric field which is induced inside the spheres by the overlapping of the double layers was not taken into account, since the interaction of semi-infinite plates was employed in the use of Derjaguin's method. In previous papers (7–9) we considered the double layer interaction of two parallel plates of finite thickness at constant surface charge density, and showed that the influence of the field induced within the plates becomes important for small plate separations. For the calculation of the double layer interaction of spheres with constant surface charge density, the interaction of plates of finite thickness should be employed in the use of Derjaguin's method. Derjaguin's method, however, becomes less accurate for large particle separations. McCartney and Levine (10) and Bell, Levine and McCartney (11) have recently calculated the potential energy of the double layer interaction between two spheres with constant surface charge density. The two spheres may have unequal surface charge densities, dielectric constants and radii. For small particle separations we obtain the potential energy of the interaction from that of plates of finite thickness by Derjaguin's method. For separations where the influence of the field inside the spheres may be neglected, we calculate the potential energy by solving an integral equation which corresponds to the Neumann problem for the Debye-Hückel equation. Finally, by combining the expression obtained by the integral equation method with that obtained by Derjaguin's method, we try to give an interpolation formula for the potential energy which may be suitable for all particle separations.

2. Interaction of two spheres for small separations

Consider two large spherical particles having surface charge densities $\sigma_1$, $\sigma_2$, dielectric constants $\varepsilon_1$, $\varepsilon_2$, and radii $a_1$, $a_2$, respectively, and separated by a distance $R$ between their centers $O_1$ and $O_2$ in an electrolyte solution of the di-
electric constant \( \varepsilon \) (fig. 1). At small particle separations and large radii such that

\[ x a_1 \gg 1, \quad x a_2 \gg 1, \quad [1] \]

\( x \) being the Debye-Hückel parameter, we can use Derjaguin’s method, which is based on the assumption that the interaction between two spheres may be formed by the contributions of pairs of infinitesimal parallel rings with flat sections. The potential energy \( V \) of the double layer interaction between the two spheres is then given by

\[ V = \int_0^\infty 2\pi h V_{pl}(H, d_1, d_2) \, dh, \quad [2] \]

where \( h \) is the radius of the two rings as shown in fig. 1, and \( V_{pl}(H, d_1, d_2) \) is the potential energy of the interaction per unit area between two parallel plates having surface charge densities \( \sigma_1, \sigma_2 \), dielectric constants \( \varepsilon_1, \varepsilon_2 \), and thicknesses \( d_1, d_2 \), respectively, and separated by a distance \( H \). The expression for \( V_{pl}(H, d_1, d_2) \) is given in the previous paper (8) in the form

\[ V_{pl} = 4\pi \left( \sigma_1^2 \alpha'(d_2, 2a_2) + \sigma_2^2 \alpha'(d_1, 2a_1) \right) \exp(-xH) + 2\sigma_1 \sigma_2 \]

where

\[ \alpha' = \frac{1 - x}{1 + x} \]

\[ \alpha(e_i, d_i) = \left( 1 + \frac{\varepsilon_i}{\varepsilon} \times 2a_i \right)^{-1} \quad (i = 1, 2). \quad [4] \]

The parameters \( \alpha(e_i, d_i) \) characterize the influence of the electric field induced within the plates and take values from 0 to 1. Now from fig. 1,

\[ H - H_0 = a_1 + a_2 - \sqrt{a_1^2 - h^2} - \sqrt{a_2^2 - h^2}, \]

\[ d_1 = 2\sqrt{a_1^2 - h^2}, \quad d_2 = 2\sqrt{a_2^2 - h^2}, \quad [5] \]

where \( H_0 \) is the shortest distance between the spheres. For \( h \ll a_1 \) and \( h \ll a_2 \) (these rings give important contributions), we have from [5]

\[ h dh \approx \frac{a_1 a_2}{a_1 + a_2} \, dH, \quad d_1 \approx 2a_1, \quad d_2 \approx 2a_2. \quad [6] \]

Then, [2] becomes

\[ V = \frac{2\pi a_1 a_2}{\alpha' = \left( 1 + \frac{\varepsilon_i}{\varepsilon} \times 2a_i \right)^{-1} \quad (i = 1, 2). \quad [8] \]

If, in addition to [1], the following conditions are satisfied:

\[ \alpha_1 \ll 1, \quad \alpha_2 \ll 1, \quad [9] \]

which may be of practical interest in colloid science, for the region

\[ x H_0 \gg \alpha_1 + \alpha_2, \quad [10] \]

we may approximately put \( \alpha_1 = \alpha_2 = 0 \) (or \( \bar{\alpha}_1 = \bar{\alpha}_2 = 1 \)) in [7] and then [7] reduces to

\[ V = \frac{4\pi^2 a_1 a_2}{\alpha' = \left( 1 + \frac{\varepsilon_i}{\varepsilon} \times 2a_i \right)^{-1} \quad (i = 1, 2). \quad [8] \]

This agrees with the expression obtained by employing the interaction of semi-infinite plates in the use of Derjaguin’s method (3). Hence we