

Approximate analytic expressions for the electrostatic interaction energy between two colloidal particles based on the modified Poisson-Boltzmann equation

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Abstract Simple analytic expressions are derived for the electrostatic interaction energy between two charged colloidal particles in an electrolyte solution. The obtained expressions are based on an approximate form of the modified Poisson-Boltzmann equation taking into account the ion size effects through Carnahan-Starling activity coefficients of electrolyte ions. We derive the electrostatic interaction energy between two parallel plates on the basis of the linear superposition approximation. We further employ Derjaguin's approximation to derive the corresponding expressions for the electrostatic interaction energy between two spheres, two parallel cylinders, or two crossed cylinders.

Keywords Electrostatic interaction energy · Modified Poisson-Boltzmann equation · Effects of ionic size · Linear superposition approximation

Introduction

According to the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory of colloid stability, the calculation of the electrostatic double-layer interaction force and energy between two charged particles in an electrolyte solution is based on the solution to the Poisson-Boltzmann equation for the electric potential distribution around the interacting particles [1–9]. The standard Poisson-Boltzmann equation, however, assumes

that ions behave like point-charges and neglects the effects of ionic size. There are many theoretical studies on the modified Poisson-Boltzmann equation [10–16], which takes into account the effect of ionic size by introducing the activity coefficients of electrolyte ions [10, 17–19]. In a previous paper [20], on the basis of the equation for the ionic activity coefficients given by Carnahan and Starling [19], which is the most accurate among existing theories, we presented a simple algorithm for solving the modified Poisson-Boltzmann equation and derived a simple approximate analytic expression for the surface charge density/surface potential relationship for a planar charged surface.

In the present paper, we present a simple algorithm for the calculation of the interaction energy between two charged colloidal particles, that is, two parallel plates, spheres, and parallel or crossed cylinders on the basis of the modified Poisson-Boltzmann equation taking into account the ion size effects through Carnahan-Starling activity coefficients of electrolyte ions [20]. In this modified Poisson-Boltzmann equation [20], we consider only the steric interactions among ions of finite size and do not consider other effects relating to the dielectric permittivity of the electrolyte solution. We employ the linear superposition approximation for the electric potential between the two interacting plates [1, 2, 7, 8, 21–23] and Derjaguin's approximation [24–26], which enables the calculation of the interaction energy between two spheres or cylinders from the corresponding interaction energy between two parallel plates. These approximations are widely used in theories of colloid stability including the original DLVO theory. Expressions for the interaction energy obtained with the help of the linear superposition approximation, which do not depend on the type of the electrostatic double-layer interaction, can be applied irrespective of whether the surface potential or the surface charge density of the interacting particles remains constant during interaction.

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Potential distribution around a single planar plate based on the modified Poisson-Boltzmann equation

The linear superposition approximation uses a potential distribution for a single plate. Before considering two parallel plates, we thus treat a single charged plate immersed in a symmetrical electrolyte solution of valence z and bulk concentration (number density) n (in units of m^{-3}) and take an x -axis perpendicular to the plate surface with its origin 0 at the plate surface so that the region $x > 0$ corresponds to the electrolyte solution. We denote the surface potential of the plate by ψ_0 . The electric potential distribution $\psi(x)$ obeys the Poisson equation for the region $x > 0$, viz.,

$$\frac{d^2\psi}{dx^2} = -\frac{\rho_{\text{el}}(x)}{\varepsilon_r\varepsilon_0} \quad (1)$$

Here, ε_r is the relative permittivity of the electrolyte solution, ε_0 is the permittivity of a vacuum, and $\rho_{\text{el}}(x)$ is the space charge density resulting from the electrolyte ions and is given by

$$\rho_{\text{el}}(x) = ze\{n_+(x) - n_-(x)\} \quad (2)$$

where $n_+(x)$ and $n_-(x)$ are, respectively, the concentrations of cations and anions at position x and e is the elementary electric charge. The boundary conditions are

$$\psi(0) = \psi_0, \psi(x) \rightarrow 0 \text{ and } \frac{d\psi}{dx} \rightarrow 0 \text{ as } x \rightarrow \infty \quad (3)$$

We assume that the activity coefficients of cations and anions at position x have the same value $\gamma(x)$. The electrochemical potential $\mu_+(x)$ of cations and that of anions $\mu_-(x)$ are thus given by

$$\mu_{\pm}(x) = \mu_{\pm}^0 \pm ze\psi(x) + kT \ln[\gamma(x)n_{\pm}(x)] \quad (4)$$

where μ_{\pm}^0 are the constant terms, k is the Boltzmann's constant, and T is the absolute temperature. The values of $\mu_{\pm}(x)$ must be the same as those in the bulk solution phase, where $\psi(x) = 0$, viz.,

$$\mu_{\pm}(\infty) = \mu_{\pm}^0 + kT \ln(\gamma^{\infty}n) \quad (5)$$

where $\gamma^{\infty} = \gamma(\infty)$. By equating $\mu_{\pm}(x) = \mu_{\pm}(\infty)$, we obtain

$$n_{\pm}(x) = \frac{\gamma^{\infty}n}{\gamma(x)} \exp\left(\mp \frac{ze\psi(x)}{kT}\right) \quad (6)$$

so that Eq. (2) gives

$$\begin{aligned} \rho_{\text{el}}(x) &= \frac{\gamma^{\infty}}{\gamma(x)} zen \left\{ \exp\left(-\frac{ze\psi(x)}{kT}\right) - \exp\left(\frac{ze\psi(x)}{kT}\right) \right\} \\ &= -\frac{2\gamma^{\infty}}{\gamma(x)} zen \sinh\left(\frac{ze\psi(x)}{kT}\right) \end{aligned} \quad (7)$$

Thus Eq. (1) becomes the following modified Poisson-Boltzmann equation:

$$\frac{d^2\psi}{dx^2} = \frac{2zen}{\varepsilon_r\varepsilon_0} \cdot \frac{\gamma^{\infty}}{\gamma(x)} \sinh\left(\frac{ze\psi(x)}{kT}\right) \quad (8)$$

When $\gamma(x) = \gamma^{\infty} = 1$, Eq. (8) becomes the following standard Poisson-Boltzmann equation:

$$\frac{d^2\psi}{dx^2} = \frac{2zen}{\varepsilon_r\varepsilon_0} \sinh\left(\frac{ze\psi(x)}{kT}\right) \quad (9)$$

We now assume that cations and anions have the same radius a . We introduce the volume fraction ϕ_+ of cations and that of anions ϕ_- at position x . Then we have

$$\phi_{\pm}(x) = \left(\frac{4}{3}\pi a^3\right)n_{\pm}(x) \quad (10)$$

The total ion volume fraction $\phi(x)$ at position x is thus given by

$$\phi(x) = \phi_+(x) + \phi_-(x) = \left(\frac{4}{3}\pi a^3\right)\{n_+(x) + n_-(x)\} \quad (11)$$

From Eq. (11), we obtain

$$\phi(x) = \frac{\phi_B\{n_+(x) + n_-(x)\}}{2n} \quad (12)$$

where $\phi_B \equiv \phi(\infty) = (4\pi a^3/3)2n$ is the total ion volume fraction in the bulk solution phase. By substituting Eq. (6) into Eq. (12), we obtain

$$\phi(x) = \phi_B \frac{\gamma^{\infty}}{\gamma(x)} \cosh\left(\frac{ze\psi(x)}{kT}\right) \quad (13)$$

The modified Poisson-Boltzmann equation (8) becomes, by using Eq. (13)

$$\frac{d^2\psi}{dx^2} = \frac{2zen}{\varepsilon_r\varepsilon_0} \cdot \frac{\phi(x)}{\phi_B} \tanh\left(\frac{ze\psi(x)}{kT}\right) \quad (14)$$

Now, we employ the expression for $\gamma(x)$ derived by Carnahan and Starling [19], viz.,

$$\gamma(x) = \exp\left[\frac{\phi(x)\{8 - 9\phi(x) + 3\phi^2(x)\}}{\{1 - \phi(x)\}^3}\right] \quad (15)$$

Then Eq. (13) becomes

$$\phi(x) = \phi_B \exp\left[-\left(\frac{\phi(x)\{8 - 9\phi(x) + 3\phi^2(x)\}}{\{1 - \phi(x)\}^3} - \frac{\phi_B(8 - 9\phi_B + 3\phi_B^2)}{(1 - \phi_B)^3}\right)\right] \cosh\left(\frac{ze\psi(x)}{kT}\right) \quad (16)$$

which is an equation for $\phi(x)$ for the given values of ϕ_B and $\psi(x)$.

In a previous paper [20], we have shown that Eq. (16) can be approximated well by

$$\phi(x) = \phi_B \frac{(1 + 8\phi_B)\cosh(ze\psi(x)/kT)}{1 + 8\phi_B\cosh(ze\psi(x)/kT)} \tag{17}$$

or equivalently

$$\gamma(x) = \gamma^\infty \frac{1 + 8\phi_B\cosh(ze\psi(x)/kT)}{1 + 8\phi_B} \tag{18}$$

which results from Eq. (13). By substituting Eq. (17) into Eq. (14), we obtain the following approximation to the modified Poisson-Boltzmann equation [20]:

$$\frac{d^2\psi}{dx^2} = \frac{2zen}{\epsilon_r\epsilon_0} \cdot \frac{\sinh\left(\frac{ze\psi(x)}{kT}\right)}{1 + \left(\frac{16\phi_B}{1 + 8\phi_B}\right)\sinh^2\left(\frac{ze\psi(x)}{2kT}\right)} \tag{19}$$

The above approximation (Eq. (19)) is a good approximation with negligible errors for low ϕ_B ($\phi_B < 0.1$) and low-to-moderate potentials ($|ze\psi_0/kT| \leq 3$). It is also to be noted that Eq. (19), which uses the Carnahan-Starling equation, differs from the so far proposed modified Poisson-Boltzmann equation based on the less precise Bikerman equation [17], in which “ $2\phi_B$ ” appears instead of “ $16\phi_B/(1 + 8\phi_B)$ ” on the right-hand side of Eq. (19).

The modified Poisson-Boltzmann equation (19) can be integrated to give

$$\kappa x = \text{sgn}(\psi_0) \sqrt{\frac{4\phi_B}{1 + 8\phi_B}} \int_y^{y_0} \frac{dy}{\sqrt{\ln\left[1 + \left(\frac{16\phi_B}{1 + 8\phi_B}\right)\sinh^2\left(\frac{y}{2}\right)\right]}} \tag{20}$$

where $\text{sgn}(\psi_0) = 1$ if $\psi_0 > 0$ and -1 if $\psi_0 < 0$, $y(x) = ze\psi(x)/kT$ is the scaled potential, $y_0 = ze\psi_0/kT$ is the scaled surface potential, and

$$\kappa = \left(\frac{2z^2e^2n}{\epsilon_r\epsilon_0kT}\right)^{1/2} \tag{21}$$

is the Debye-Hückel parameter. Equation (20) gives $y(x)$ as a function of the scaled distance κx . It can be shown that at large distances x compared with the Debye length $1/\kappa$, the asymptotic form of $\psi(x)$ must be

$$\psi(x) = \psi_{\text{eff}} e^{-\kappa x} \tag{22}$$

where ψ_{eff} is called the effective surface potential and is related to the surface potential ψ_0 by [23]

$$\psi_{\text{eff}} = \psi_0 \exp\left[\int_0^{y_0} \left\{\frac{1}{f(y)} - \frac{1}{y}\right\} dy\right] \tag{23}$$

with

$$f(y) = \text{sgn}(\psi_0) \sqrt{\frac{1 + 8\phi_B}{4\phi_B}} \sqrt{\ln\left[1 + \left(\frac{16\phi_B}{1 + 8\phi_B}\right)\sinh^2\left(\frac{y}{2}\right)\right]} \tag{24}$$

Equation (23) as combined with Eq. (24) will be used later. Note that at $\phi_B = 0$, Eqs. (23) and (24) give

$$\psi_{\text{eff}} = \frac{4kT}{ze} \tanh\left(\frac{ze\psi_0}{4kT}\right) \tag{25}$$

which agrees with the result obtained via the standard Poisson-Boltzmann equation (8).

Electrostatic interaction between two parallel plates

Consider two parallel plates 1 and 2 having surface potentials ψ_1 and ψ_2 , respectively, in the absence of interaction, separated by h between their surfaces in a symmetrical electrolyte solution of valence z and bulk concentration (number density) n (in units of m^{-3}) and take an x -axis perpendicular to the plate surface with its origin 0 of plate 1 (Fig. 1a). The electrostatic interaction force $P_{\text{pl}}(h)$ per unit area between plates 1 and 2 can be calculated by integrating the osmotic pressure and the Maxwell stress over an arbitrary closed surface Σ enclosing either one of the two interacting plates. As Σ , we choose two planes located at $x = -\infty$ (in the bulk solution far from the plates) and $x = x'$ ($0 < x' < h$) enclosing plate 1. Here, x' is an arbitrary point near the midpoint in the region $0 < x < h$ between plates 1 and 2.

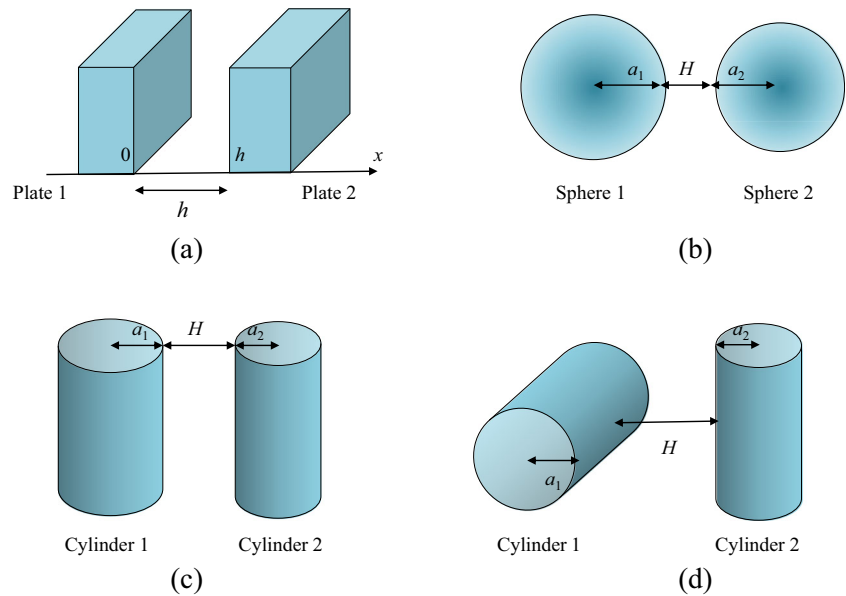
At equilibrium, the gradient of the pressure $p(x)$ and the electric force $\rho_{\text{el}}(x)d\psi(x)/dx$ acting on the space charge $\rho_{\text{el}}(x)$ must balance each other, viz.,

$$\frac{dp(x)}{dx} + \rho_{\text{el}}(x) \frac{d\psi}{dx} = 0 \tag{26}$$

By substituting the Poisson equation (1) into Eq. (26), we obtain

$$\frac{d}{dx} \left[p(x) - \frac{1}{2} \epsilon_r \epsilon_0 \left(\frac{d\psi}{dx}\right)^2 \right] = 0 \tag{27}$$

Fig. 1 Interaction between two colloidal particles at separation h or H between their surfaces. Parallel plates (a). Spheres (b). Parallel cylinders (c). Crossed cylinder (d)



which gives

$$p(x) - \frac{1}{2} \varepsilon_r \varepsilon_0 \left(\frac{d\psi}{dx} \right)^2 = \text{constant} \quad (28)$$

The second term on the left-hand side of Eq. (28) corresponds to the Maxwell stress. The pressure $p(x)$ at position x can be obtained from the Gibbs-Duhem relation [11], viz.,

$$n_+(x) \frac{d\mu_+(x)}{dx} + n_-(x) \frac{d\mu_-(x)}{dx} = 0 \quad (29)$$

By substituting Eq. (4) into Eq. (29), we obtain

$$kT \frac{d}{dx} \{n_+(x) + n_-(x)\} + kT \{n_+(x) + n_-(x)\} \frac{d \ln \gamma(x)}{dx} + \rho_{el}(x) \frac{d\psi(x)}{dx} = 0 \quad (30)$$

By comparing Eqs. (26) and (30), we find [11]

$$\frac{dp(x)}{dx} = kT \frac{d}{dx} \{n_+(x)^+ + n_-(x)^-\} + kT \{n_+(x)^+ + n_-(x)^-\} \frac{d \ln \gamma(x)}{dx} \quad (31)$$

which can be integrated to give

$$p(x) = kT \{n_+(x) + n_-(x)\} + kT \int \{n_+(x) + n_-(x)\} \frac{d \ln \gamma(x)}{dx} dx + \text{constant} \quad (32)$$

The first term on the right-hand side of Eq. (32) is the usual osmotic pressure obtained via the standard Poisson-Boltzmann equation (9) and the second term results from the effect of ionic size. The sum of the first and second terms on

the right-hand side of Eq. (32) corresponds to the osmotic pressure of electrolyte ions taking into account the ionic size effect. Now, we substitute Eqs. (17) and (18) into Eq. (32) to obtain

$$p(x) = 2nkT \left\{ 1 + \left(\frac{1 + 8\phi_B}{8\phi_B} \right) \ln \left(\frac{1 + 8\phi_B \cosh y}{1 + 8\phi_B} \right) \right\} + p_0 \quad (33)$$

where p_0 is the pressure in the absence of electrolyte ions. The electrostatic interaction force per unit area between plates 1 and 2 is thus given by

$$P_{pl}(h) = \left[p(x) - \frac{1}{2} \varepsilon_r \varepsilon_0 \left(\frac{d\psi(x)}{dx} \right)^2 \right]_{x=x'} - \left[p(x) - \frac{1}{2} \varepsilon_r \varepsilon_0 \left(\frac{d\psi(x)}{dx} \right)^2 \right]_{x=-\infty} \quad (34)$$

By substituting Eq. (33) into Eq. (34), we obtain

$$P_{pl}(h) = 4nkT \left(\frac{1 + 8\phi_B}{16\phi_B} \right) \ln \left[1 + \left(\frac{16\phi_B}{1 + 8\phi_B} \right) \sinh^2 \left(\frac{ze\psi(x')}{2kT} \right) \right] - \frac{1}{2} \varepsilon_r \varepsilon_0 \left(\frac{d\psi}{dx} \Big|_{x=x'} \right)^2 \quad (35)$$

Here, we have used the fact that $p(-\infty) = 2nkT + p_0$ and $d\psi/dx = 0$ at $x = -\infty$. Since x' is an arbitrary point near the midpoint in the region $0 < x < h$ between plates 1 and 2, $\psi(x')$ can be considered to be small so that

Eq. (35) can be linearized with respect to $\psi(x')$ to give

$$P_{pl}(h) = \frac{1}{2} \varepsilon_r \varepsilon_0 \left\{ \kappa^2 \psi^2(x') - \left(\frac{d\psi}{dx} \Big|_{x=x'} \right)^2 \right\} \quad (36)$$

Here, $P_{pl}(h) > 0$ corresponds to repulsion and $P_{pl}(h) < 0$ to attraction. It must be stressed that the above linearization is not for the surface potentials ψ_1 and ψ_2 but only for $\psi(x')$. That is, this linearization approximation holds good even when the surface potentials are arbitrary, provided that the particle separation h is large compared with the Debye length $1/\kappa$. Also in this region, $\psi(x')$ can be approximated as the sum of the asymptotic forms of the unperturbed potentials $\psi_1(x')$ and $\psi_2(x')$ produced by plates 1 and 2, respectively, in the absence of interaction, which are given by Eq. (22), viz.,

$$\psi(x') = \psi_1(x') + \psi_2(x') \tag{37}$$

with

$$\psi_1(x') = \psi_{eff1} e^{-\kappa x'} \tag{38}$$

$$\psi_2(x') = \psi_{eff2} e^{-\kappa(h-x')} \tag{39}$$

where ψ_{eff1} and ψ_{eff2} are, respectively, the effective surface potentials of plates 1 and 2. These potentials are given by Eq. (23) as combined with Eq. (24). By substituting Eqs. (37)–(39) into Eq. (36), we obtain

$$P_{pl}(h) = 2\varepsilon_r\varepsilon_0\kappa^2\psi_{eff1}\psi_{eff2}e^{-\kappa h} \tag{40}$$

Note that $P(h)$ is independent of the value of x' . The electrostatic interaction energy $V_{pl}(h)$ per unit area between plates 1 and 2 can thus be derived by integrating Eq. (40), viz.,

$$V_{pl}(h) = 2\varepsilon_r\varepsilon_0\kappa\psi_{eff1}\psi_{eff2}e^{-\kappa h} \tag{41}$$

Equation (41) as combined with Eqs. (23) and (24) is the required expression for the electrostatic interaction energy between two parallel plates 1 and 2 based on the modified Poisson-Boltzmann equation (19) taking into account the ion size effect.

Results and discussion

We have derived an approximate expression (41) for the interaction energy per unit area between two parallel plates. This expression, which is based on the linear superposition approximation, involves the effective surface potential calculated with Eqs. (23) and (24). It is to be noted that the expressions for the interaction force and energy based on the modified Poisson-Boltzmann equation (8) takes the same form as those based on the standard Poisson-Boltzmann equation (9). The difference is that the effective surface potentials appearing in these expressions are given by Eqs. (23) and (24) for the modified Poisson-Boltzmann equation case but they are given by Eq. (25) for the standard Poisson-Boltzmann equation case.

With the help of Derjaguin’s approximation [24], one can calculate the electrostatic interaction energy $V_{sp}(H)$ between two spheres 1 and 2 having radii a_1 and a_2 and effective surface potentials ψ_{eff1} and ψ_{eff2} , respectively, separated by a distance H between their surfaces (Fig. 1b) via the corresponding electrostatic interaction energy $V_{pl}(h)$ between two parallel dissimilar plates, viz.,

$$V_{sp}(H) = \frac{2\pi a_1 a_2}{a_1 + a_2} \int_H^\infty V_{pl}(h) dh \tag{42}$$

By substituting Eq. (41) into Eq. (42), we obtain

$$V_{sp}(H) = \frac{4\pi a_1 a_2}{a_1 + a_2} \varepsilon_r\varepsilon_0\psi_{eff1}\psi_{eff2}e^{-\kappa H} \tag{43}$$

Similarly, by using Derjaguin’s approximation for the electrostatic interaction energy $V_{cy//}(H)$ per unit length between two parallel cylinders having radii a_1 and a_2 and effective surface potentials ψ_{eff1} and ψ_{eff2} , respectively, separated by a distance H between their surfaces [25, 26], that is,

$$V_{cy//}(H) = \sqrt{\frac{2a_1 a_2}{a_1 + a_2}} \int_H^\infty V_{pl}(h) \frac{dh}{\sqrt{h-H}} \tag{44}$$

we obtain

$$V_{cy//}(H) = 2\sqrt{\frac{2\pi a_1 a_2}{a_1 + a_2}} \sqrt{\kappa\varepsilon_r\varepsilon_0\psi_{eff1}\psi_{eff2}} e^{-\kappa H} \tag{45}$$

For the case of two crossed cylinders having radii a_1 and a_2 and effective surface potentials ψ_{eff1} and ψ_{eff2} , respectively, at separation H between their closest surfaces, Derjaguin’s approximation for the interaction energy $V_{cy\perp}(H)$ is given by [25, 26]

$$V_{cy\perp}(H) = 2\pi\sqrt{a_1 a_2} \int_H^\infty V_{pl}(h) dh \tag{46}$$

By substituting Eq. (42) into Eq. (46), we obtain

$$V_{cy\perp}(H) = 4\pi\sqrt{a_1 a_2} \varepsilon_r\varepsilon_0\psi_{eff1}\psi_{eff2}e^{-\kappa H} \tag{47}$$

The scaled interaction energies for the above four cases take the same functional form, that is, $V^*(h) = y_{eff1}y_{eff2}e^{-\kappa h}$ for two parallel plates and $V^*(H) = y_{eff1}y_{eff2}e^{-\kappa H}$ for two spheres and two parallel or crossed cylinders. That is,

$$V^*(h) \equiv \left(\frac{ze}{kT}\right)^2 \left(\frac{1}{2\varepsilon_r\varepsilon_0\kappa}\right) \cdot V_{pl}(h) = y_{eff1}y_{eff2}e^{-\kappa h} \tag{48}$$

$$V^*(H) \equiv \left(\frac{ze}{kT}\right)^2 \left(\frac{a_1 + a_2}{4\pi\varepsilon_r\varepsilon_0 a_1 a_2}\right) \cdot V_{sp}(H) = y_{eff1}y_{eff2}e^{-\kappa H} \tag{49}$$

$$V^*(H) \equiv \left(\frac{ze}{kT}\right)^2 \frac{1}{2\varepsilon_r\varepsilon_0} \sqrt{\frac{a_1 + a_2}{2\pi a_1 a_2 \kappa}} V_{cy//}(H) \\ = y_{\text{eff}1} y_{\text{eff}2} e^{-\kappa H} \quad (50)$$

and

$$V^*(H) \equiv \left(\frac{ze}{kT}\right)^2 \left(\frac{1}{4\pi\varepsilon_r\varepsilon_0\sqrt{a_1 a_2}}\right) V_{cy\perp}(H) \\ = y_{\text{eff}1} y_{\text{eff}2} e^{-\kappa H} \quad (51)$$

In Fig. 2, we plot the scaled electrostatic interaction energies $V^*(h) = y_{\text{eff}}^2 e^{-\kappa h}$ or $V^*(H) = y_{\text{eff}}^2 e^{-\kappa H}$ for two similar parallel plates, two similar spheres, or two similar cylinders having scaled surface potential $y_o = ze\psi_o/kT$ and scaled effective surface potential $y_{\text{eff}} = ze\psi_{\text{eff}}/kT$ as a function of κh or κH for $y_o = 1, 2$, and 3 at $\phi_B = 0, 0.05$, and 0.1. Figure 2 shows how the effects of ionic size on the electrostatic interaction energy become appreciable for a higher surface potential y_o and a higher total ion volume fraction ϕ_B . For $y_o = 2$ and $\phi_B = 0.05$ for example, the modified Poisson-Boltzmann equation (Eq. (8)) gives $V^*(\kappa h)$ (or $V^*(\kappa H)$) = 1.449, while the standard Poisson-Boltzmann equation (Eq. (9)) gives $V^*(\kappa h)$ (or $V^*(\kappa H)$) = 1.257, the difference being 15%. The ionic size effect always gives rise to an increase in the interaction energy $V^*(\kappa h)$ (or $V^*(\kappa H)$). This is because the ionic

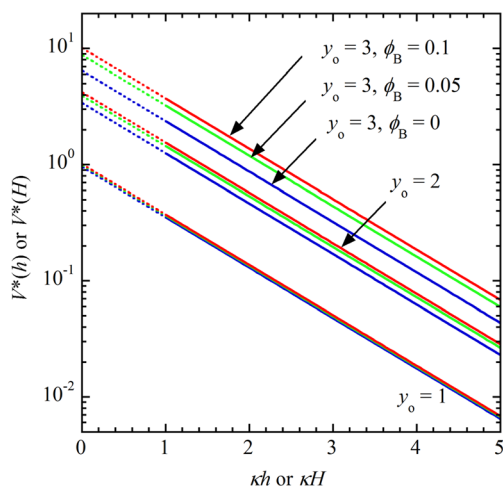


Fig. 2 Scaled electrostatic interaction energy $V^*(h) = y_{\text{eff}}^2 e^{-\kappa h}$ for two parallel similar plates and $V^*(H) = y_{\text{eff}}^2 e^{-\kappa H}$ for two similar spheres of radius a and for two parallel or crossed similar cylinders of radius a . Calculated with Eqs. (48)–(51) with $a_1 = a_2 = a$ and $y_{\text{eff}1} = y_{\text{eff}2} = y_{\text{eff}}$ for the scaled unperturbed surface potential $y_o = 1, 2$, and 3 at the total ion volume fraction $\phi_B = 0, 0.05$, and 0.1. The lines for $\phi_B = 0$ correspond to the results obtained via the standard Poisson-Boltzmann model neglecting the ionic size effect. For small κh or κH , the linear superposition approximation (LSA) is no longer good approximation and thus the energy curves are given by dotted lines $\kappa h \leq 1$ or $\kappa H \leq 1$. Note that the scaled interaction energy takes the same functional form $V^*(h) = y_{\text{eff}}^2 e^{-\kappa h}$ for plates or $V^*(H) = y_{\text{eff}}^2 e^{-\kappa H}$ for spheres and cylinders

concentration becomes lower due to the ionic size effect, leading to a decrease in the ionic shielding effects so that the magnitude of $V^*(\kappa h)$ (or $V^*(\kappa H)$) increases.

It is to be noted that the expressions for the interaction energy $V(\kappa h)$ or $V(\kappa H)$ between the two particles obtained in the present paper are derived on the basis of the linear superposition approximation (LSA). This approximation is no longer a good approximation for small particle separations h or H as compared with the Debye length $1/\kappa$ and thus the energy curves are given by dotted lines in Fig. 2. The interaction force and energy between two particles for small particle separations depend on the interaction models. Most generally employed models are the constant surface potential model and the constant surface charge density model, where the surface potential ψ_o or surface charge density σ of the particles remain constant during interaction. In the appendix we give the exact expressions for the interaction force between two parallel similar plates obtained from the constant surface potential model and the constant surface charge density model. It is known that the magnitude of the interaction energy or force obtained from the linear superposition approximation lies between those obtained from the above two interaction models and a good approximation for $\kappa h > 1$ or $\kappa H > 1$ [7]. For this reason, the linear superposition approximation is employed in the original DLVO theory of the stability of colloidal suspensions [1, 2]. Indeed, Eq. (43) with $a_1 = a_2$ and $y_{\text{eff}1} = y_{\text{eff}2}$ for the case $\phi_B = 0$ is employed in the original DLVO theory [1, 2]. Equation (43) is thus a generalization of the DLVO electrostatic interaction energy by taking into account the ion size effects.

Conclusion

We have presented a simple algorithm for calculating the electrostatic interaction energy between two charged particles (plates, spheres, and cylinders) in an electrolyte solution based on the modified Poisson-Boltzmann equation (8) for the electric potential around the interacting particles, which takes into account the effects of ionic size on the basis of ionic activity coefficient given by Carnahan and Starling. It is to be noted that expressions for the interaction force and energy based on the modified Poisson-Boltzmann equation [8] takes the same form as those based on the standard Poisson-Boltzmann equation [9]. The difference is that the effective surface potentials $\psi_{\text{eff}1}$ and $\psi_{\text{eff}2}$ appearing in these expressions are different for these two cases. In a previous paper [27], we derived a simple expression for the stability ratio of colloidal dispersions by considering the sum of the electrostatic and van der Waals interaction energies between two spherical

particles based on the standard Poisson-Boltzmann equation [9]. By replacing the expressions for the effective surface potentials appearing in the electrostatic interaction energy with those based on the modified Poisson-Boltzmann equation (8), the ionic size effect is taken into account in the resultant electrostatic energy expression.

Compliance with ethical standards

Conflict of interest The author declares that he has no conflict of interest.

Source of funding The author declares no sources of funding.

Appendix

Analytic expressions for the interaction between two parallel similar plates at separation h can be derived on the basis of the modified Poisson-Boltzmann equation (19). The interaction force $P_{pl}(h)$ per unit area between the two plates is given by

$$P_{pl}(h) = 4nkT \frac{1}{g(\phi_B)} \ln \left[1 + g(\phi_B) \sinh^2 \left(\frac{y_m}{2} \right) \right] \quad (52)$$

with

$$g(\phi_B) = \frac{16\phi_B}{1 + 8\phi_B} \quad (53)$$

where y_m is the scaled potential at the midpoint $x = h/2$ between the two plates. Eq. (52) can be derived from Eq. (35) by choosing $h/2$ as x' . Note that Eq. (52) can be applied for both of the constant surface potential and surface charge density models. For the constant surface potential model, y_m is related to the scaled surface potential $y_o = ze\psi_o/kT$, viz.,

$$\kappa h = \sqrt{g(\phi_B)} \int_{|y_m|}^{|y_o|} \frac{dy}{\sqrt{\ln \left[\frac{1 + g(\phi_B) \sinh^2(y/2)}{1 + g(\phi_B) \sinh^2(y_m/2)} \right]}} \quad (54)$$

which is derived by applying Eq. (20) for the system of two parallel plates. For the constant surface charge density model, on the other hand, we have

$$\kappa h = \sqrt{g(\phi_B)} \int_{|y_m|}^{|y(0)|} \frac{dy}{\sqrt{\ln \left[\frac{1 + g(\phi_B) \sinh^2(y/2)}{1 + g(\phi_B) \sinh^2(y_m/2)} \right]}} \quad (55)$$

Note that the scaled surface potential $y(0)$, which is a function of the plate separation h , is related to the scaled

unperturbed surface potential $y_o = ze\psi_o/kT$ in the absence of interaction ($h = \infty$) by

$$\sigma^2 = \left(\frac{2\varepsilon_r \varepsilon_o \kappa kT}{ze} \right)^2 \frac{1}{g(\phi_B)} \ln \left[\frac{1 + g(\phi_B) \sinh^2(y(0)/2)}{1 + g(\phi_B) \sinh^2(y_m/2)} \right] \quad (56)$$

which can be derived by integrating Eq. (19) once and applying the boundary condition: $d\psi/dx|_{x=0^+} = -\sigma/\varepsilon_r \varepsilon_o$ and $d\psi/dx|_{x=h/2} = 0$ (from symmetry of the system). The surface charge density σ of the plates is related to the scaled unperturbed surface potential $y_o = ze\psi_o/kT$ (in the absence of interaction) by

$$\sigma = \text{sgn}(\psi_o) \frac{2\varepsilon_r \varepsilon_o \kappa kT}{ze} \sqrt{\frac{1}{g(\phi_B)} \cdot \ln \left[1 + g(\phi_B) \sinh^2 \left(\frac{y_o}{2} \right) \right]} \quad (57)$$

By combining Eqs. (56) and (57), we obtain

$$1 + g(\phi_B) \sinh^2(y_o/2) = \frac{1 + g(\phi_B) \sinh^2(y(0)/2)}{1 + g(\phi_B) \sinh^2(y_m/2)} \quad (58)$$

Equations (55) and (58) form coupled equations for y_m for the given values of y_o and κh .

Once the value of y_m is obtained from Eq. (54) for the constant potential model (in which $y(0)$ is always equal to the unperturbed surface potential y_o) or the coupled Eqs. (55) and (58) for the constant surface charge density model, one can calculate the interaction force $P_{pl}(h)$ via Eq. (52).

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