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ORIGINAL CONTRIBUTION

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Improvement on the Derjaguin's method for the interaction of spherical particles

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Abstract A correction to the classical Derjaguin's method has been given for the electrical double layer interaction of two spherical particles. Simple analytic expressions are given. Results obtained respectively for identical and dissimilar spherical particles show that the expressions open up the usable area of familiar Derjaguin's formulas.

Key words DLVO theory – Derjaguin method – repulsive energy – spheres

Derjaguin [1] has indicated how the interaction of two spheres can be calculated from the interaction of two parallel plates. His equation is one of general applicability, provided the thickness of the double layer is small compared with the radius of the sphere. Derjaguin himself has used this approximation to calculate the repulsive energy of the two identical spheres at small surface potential. Hogg–Healy–Fuerstenau [2] (HHF) used the Derjaguin approximation for deriving the interaction free energy between dissimilar spheres. However, apart from the influence of actual curvature of the field lines, the classical Derjaguin result, and thus HHF formula, give higher values for the electrostatic repulsive energy. Chan and White [3], Ohshima, Chan, Healy and White (OCHW) [4] have suggested that next-order correction terms to HHF formula should be of the order of $(1/\kappa\ a_i)$, where κ is Debye–Hückel parameter and a_i is the radius of sphere i ($i = 1, 2$). OCHW showed that HHF result is the correct leading-order expression for the interaction energy between unequal spheres, and derived the next-order correction to the HHF formula. Though their expression is only the first term in an expansion in power of $(\kappa\ a_i)^{-1}$. However, it is somewhat tediously long. When the particles are far apart and the double layer overlap is relatively weak the linear superposition approximation [5] is available as approximate expression, which gives the correct behaviour at large κH (H is a closest separation between spheres). Recently, accurate results are obtained using a two-center expansion for the solution of the linearized PB equation and numerical implementations of the algorithm are given for a full range of particles size, κa, and particles separations, κH [6]. However, the results are only implemented on the computer.

This paper attempts to present a simple curvature correction method which is capable of deriving approximate expressions for electrostatic interaction energy with Derjaguin method. The expressions have simple analytic form and high accuracy for any κa and κH within the limits of linear approximation.

In Derjaguin's method the interaction between spheres is supposed to be built up from the interaction of pairs of rings with radius h, thickness dh at a distance H, the rings

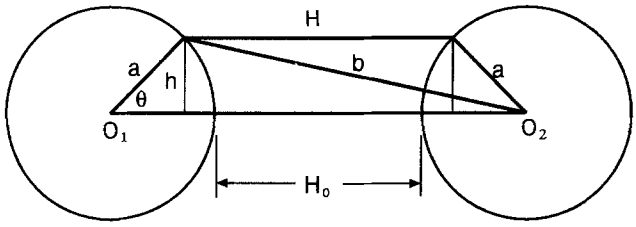


Fig. 1 Geometrical construction used in the calculation of interaction between two identical spherical particles, radius a from the interaction of two infinite flat plates

interaction as if they were parallel flat surfaces with same area and distance as illustrated in Fig. 1 and in the Eq. (1)

$$V_R = \int_0^\infty 2\pi h \cdot V(\text{flat}) dh \tag{1}$$

$$H - H_0 = 2(a - \sqrt{a^2 - h^2}) , \tag{2}$$

then

$$a(1 - h^2/a^2)^{1/2} dH = 2hdh , \tag{3}$$

or approximately

$$2hdh = a(1 - h^2/2a^2 - h^4/8a^4 - \ldots\ldots) dH . \tag{4}$$

If $a \gg h$, the above expression will be very well approximated as $2hdh = adH$, it is the case of Derjaguin treatment. If κa is not very large, Overbeek [7] has taken into account that most of the interaction takes place at $\kappa^2 h^2 < 2\kappa a$; thus, Eq. (4) can be slightly improved to

$$2hdh = a(1 - 1/2\kappa a) dH . \tag{5}$$

Overbeek's correction improved the final results, but some problems remain to be solved, particularly, when $\kappa H > 1$ the results of Eq. (5) still hold larger. Here, we take into account an improved method. The expression (4) can be improved to be

$$2hdh = a(1 - \kappa H/2\kappa a + 1/2\kappa a) dH \tag{6}$$

Generally speaking, $H > h$, therefore, correction terms of the curvature can be read $[1 - (\kappa H - 1)/2\kappa a]$, in order to compensate the correction for a loss (see the Appendix).

An expression for the free energy of the interaction per unit area of two parallel flat double layers is [8]

$$V(\text{flat}) = 2nkTZ^2 \kappa^{-1} [1 - \tanh(\kappa H/2)] , \tag{7}$$

where n is the electrolyte concentration, k is the Boltzmann constant, T is the absolute temperature, and $Z = ve\psi_0/kT$, v and e are the valency of the electrolyte and the electric charge of proton respectively, ψ_0 is the surface potential. With this equation and that from Eq. (6) in Eq. (1), the free energy of the interaction of two identical spheres becomes

$$V_R = 2\pi\varepsilon_0\varepsilon_r a\psi_0^2 \operatorname{Ln}(1 + e^{-\kappa H})[1 - (\kappa H + \alpha_1 - 1)/2\kappa a] , \tag{8}$$

where ε_r is the relative dielectric constant of the solution and ε_0 is the premittivity of free space

$$\alpha_1 = \sum_{m=1}^{\infty} (-1)^{m+1} m^{-2} \exp(-m\kappa H)/\operatorname{Ln}[1 + e^{-\kappa H}] . \tag{9}$$

Numerical data of α_1 as a function of κH are given in Table 1.

If $\kappa H \to 0$, α_1 goes to 1.1865, obviously, $\alpha_1 - 1 \approx 0$, Eq. (8) reduces to

$$V_R = 2\pi\varepsilon_0\varepsilon_r a\psi_0^2 \operatorname{Ln}(1 + e^{-\kappa H})[1 - \kappa H/2\kappa a] \tag{10}$$

In Eq. (10) the factor $[1 - \kappa H/2\kappa a]$ can be seen that the first two terms of the expansion of $[1 + \kappa H/2\kappa a]^{-1}$

$$[1 + \kappa H/2\kappa a]^{-1} \approx 1 - \kappa H/2\kappa a , \tag{11}$$

thus

$$V_R = 4\pi\varepsilon_r\varepsilon_0 a\psi_0^2 (a/R) \operatorname{Ln}(1 + e^{-\kappa H}) , \tag{12}$$

where $R = 2a + H$.

In Table 2, we compare present results of Eq. (12) with the exact computer results by McCartney and Levine [9]. Clearly, the agreement is excellent. The maximum relative

Table 1 Values of α_1 and α_2

κH	0.1	0.5	1	2	3	4
α_1	1.1725	1.1247	1.0810	1.0322	1.0122	1.0045
α_2	0.5572	0.7908	0.8912	0.9642	0.9873	0.9954

Table 2 Comparison of present results Eq. (12) with computer results By ML for two identical spheres

κa	κH	Eq. (12)	$V/2\pi\varepsilon a\psi_0^2$ Computer Results	Error %
	0.5	0.4515	0.4477	0.8
	1	0.2848	0.2856	−0.3
5	2	0.1058	0.1061	−0.3
	3	0.0374	0.0372	0.5
	4	0.0130	0.0128	1.6
	0.5	0.4625	0.4578	1.0
	1	0.2983	0.2971	0.4
10	2	0.1154	0.1150	0.3
	3	0.0422	0.0419	0.7
	4	0.0151	0.0150	0.7
	0.5	0.4663	0.4615	1.0
	1	0.3032	0.3013	0.6
15	2	0.1190	0.1183	0.6
	3	0.0442	0.0438	0.9
	4	0.0160	0.0158	1.3

error is less than 1.6% at any κH; Eq. (12) seems to be the best approximate expression at present for determining the electrostatic repulsive energy between identical spheres. When κH is large from Eq. (12), we obtain

$$V_R = 4\pi\varepsilon_r\varepsilon_0 a\psi_0^2(a/R)e^{-\kappa H} . \tag{12a}$$

This is just the right result of the LSA [5]. It is well known that Eq. (12a) has the correct asymptotic behavior at large separation, that is, Eq. (12) also improves upon Eq. (12a) in respect to raising its accuracy at small separation. Without doubt, it retain the character of Derjaguin method, and gives good results at small κH. The utility of the improved Derjaguin approximation is that it is uniformly valid for both small and large separation.

When κa is large, a direct transformation of energy of two plates into that of two spheres is permitted; such a simple transformation has never existed when κa is small. In that case, in general, we must first calculate the electric field in the double layer around the particles, and after that the free energy of the double layers. This method was used by Verwey and Overbeek [8]. Assuming that the potential of the surface potential remains constant, the potential energy of interaction in small κa is given by

$$V_R = 4\pi\varepsilon_r\varepsilon_0 a\psi_0^2(a/R)e^{-\kappa H}\cdot\beta , \tag{13}$$

in which β is a very complicated function of κa and κH and is defined in Verwey and Overbeek's book [8]. The values of β require numerical solution of the complex equations. This has led to the extensive use of tables [8] which are available for only selected values of κa and κH. This restriction means that in most practical cases, one must interpolate from the table. Fortunately, as β is always 0.6 to 1.0, we may neglect their influence on the repulsion in many cases where no great precision is required. Thus, Eq. (13) changes into

$$V_R = 4\pi\varepsilon_r\varepsilon_0\varepsilon a\psi_0^2(a/R)e^{-\kappa H} , \tag{13a}$$

which is identical with that formula obtained by LSA [5], applicable to large particles separation. In the present work we have derived Eq. (12) with improved Derjaguin approximation; it eliminates error to a great extent. As a result, the surfaces of spheres are not parallel to each other, such that it is capable of calculating the interaction energy for small κa.

Table 3 shows the relative error between Eq. (12) and Eq. (13). Good agreement of improved Derjaguin approximation with exact expression Eq. (13) is seen in Table 3. It is to be noted that the ratio of Eq. (12) and Eq. (13) is $[\mathrm{Ln}(1+e^{-\kappa H})/\beta\cdot e^{-\kappa H}]$, and the values numerical of $\mathrm{Ln}(1+e^{-\kappa H})/e^{-\kappa H}$ is between 0.6931 (Ln2) and 1.0, and approximately equal to β, perhaps it is just as well that Eq. (12) is applicable to small κa.

Table 3 Relative error (%) of improved Derjaguin approximation Eq. (12) with Eq. (13)

κH	$\kappa a = 0.1$	$\kappa a = 1.0$	$\kappa a = 2.0$
0	12	5.5	0.6
0.2	− 12	0.3	− 1.6
0.4	− 15	− 2.8	− 3.0
1.0	− 12	− 5.5	− 4.7
2.0	− 5.7	− 3.6	− 3.1
4.0	− 0.9	0.2	− 0.6

It is well known that classical Derjaguin method is applicable to large particle radii and small particle separation, however, Eq. (12) opens up the usable area of the familiar Derjaguin formula. It can be used to obtain a better estimate of V_R for any values of κa and further separation, provided the surface potential is low.

Unlike spherical particles, Eq. (2) becomes

$$H - H_0 = a_1 + a_2 - \sqrt{a_1^2 - h^2} - \sqrt{a_2^2 - h^2}$$
$$dH = hdh[(a_1^2 - h^2)^{-1/2} - (a_2^2 - h^2)^{-1/2}] , \tag{14}$$

or approximately to

$$hdh = a_1 a_2/(a_1 + a_2)$$
$$\cdot dH[1 - h^2/2\cdot(1/a_1^2 - 1/a_1 a_2 + 1/a_2^2)] . \tag{15}$$

According to the above approximate method,

$$hdh = a_1 a_2/(a_1 + a_2)$$
$$\cdot[1 - \kappa H/4\kappa a_1 + 1/4\kappa a_1 - \kappa H/4\kappa a_2$$
$$+ 1/4\kappa a_2]dH . \tag{16}$$

For the interaction energy of repulsion between two parallel, infinite, flat double layers, one can use the convenient form obtained by HHF for constant surface potentials ψ_1 and ψ_2.

$$V(\mathrm{flat}) = \varepsilon_0\varepsilon_r\kappa/4\cdot\{(\psi_1 + \psi_2)^2[1 - \tanh(\kappa H/2)]$$
$$- (\psi_1 - \psi_2)^2[\coth(\kappa H/2) - 1]\} \tag{17}$$

Substituting Eq. (17) and Eq. (15) into Eq. (1) leads to

$$V_R = \pi\varepsilon_0\varepsilon_r a_1 a_2/(a_1 + a_2)\cdot\{\psi_1 + \psi_2)^2\,\mathrm{Ln}(1 + e^{-\kappa H})$$
$$\cdot[1 - (1/4\kappa a_1 + 1/4\kappa a_2)(\kappa H + \alpha_1 - 1)]$$
$$+ (\psi_1 - \psi_2)^2\,\mathrm{Ln}(1 - e^{-\kappa H})$$
$$\cdot[1 - (1/4\kappa a_1 + 1/4\kappa a_2)(\kappa H + \alpha_2 - 1)]\} , \tag{18}$$

where

$$\alpha_2 = -\sum_{m=1}^{\infty} m^{-2}\exp(-m\kappa H)/\mathrm{Ln}[1 - \exp(-\kappa H)]$$

The values of α_2 are given in Table 1.

It is to be noted that α_2 goes to zero if $\kappa H \to 0$. However, the convergent speed is very slow, for example, when $\kappa H = 1 \times 10^{-10}$, $\alpha_2 = 0.0673$. The corresponding approximation, $\alpha_2 - 1 \approx 0$, is obtained

$$V_R = \pi\varepsilon a_1 a_2/(a_1 + a_2)\cdot[(\psi_1 + \psi_2)^2 \operatorname{Ln}(1 + e^{-\kappa H}) - (\psi_1 - \psi_2)^2 \operatorname{Ln}(1 - e^{-\kappa H})] \cdot(1 - \kappa H/4\kappa a_1 - \kappa H/4\kappa a_2) \quad (19)$$

or

$$V_R = V_{HHF}\cdot(1 - \kappa H/4\kappa a_1 - \kappa H/4\kappa a_2) .$$

Assuming $\mathbf{a} = 2a_1 a_2/(a_1 + a_2)$ is the reduced particle radius, then

$$2V_R = [2\mathbf{a}/(2\mathbf{a} + H)]\cdot V_{HHF} . \quad (20)$$

Here, V_{HHF} is the HHF derived an equation for dissimilar spheres. Numerical computer calculations of the interaction energy between dissimilar spheres on the basis of the PB equation have not been reported. For the special case of two identical spheres, Eq. (20) reduces to Eq. (12). A good analytic expression has been obtained by OCHW for the interaction of dissimilar spheres; it is an improvement on the HHF formulas without recourse Derjaguin's method (Eq. (23) of ref. [4]). In Table 4, we compare the results of Eq. (20) with the results of OCHW. for $\kappa a_1 = 20$; $\kappa a_2 = 10$ and $\psi_2/\psi_1 = 1/2;\ -1/2$.

It is clear than Eq. (20) yields quite good results for dissimilar spherical particles. If the surface potential is low, Eq. (20) can always be very effectively applied for any κH. Due to the feature of α_2, which has a little larger deviation from 1 in $\kappa H < 1$, in the case of dissimilar spheres the error is a bit too large.

Recently, Ohshima et al. [10] suggested an exactly solvable model for electrostatic double layer interaction of two charged ion-penetrable spheres, and checked the validity of Derjaguin method. They confirm once again that Derjaguin's result is the correct leading order expression for the interaction energy and the next-order correction terms are of the order of $1/\kappa a_i$. Their exact expression reads

$$V(H) = \pi a_1 a_2 \rho_1 \rho_2/\varepsilon_r\varepsilon_0\kappa^4\cdot[e^{-\kappa H}/(H + a_1 + a_2)] \times\{1 + \exp(-2\kappa a_1) - [1 - \exp(-2\kappa a_1)]/\kappa a_1\} \times\{1 + \exp(-2\kappa a_2) - [1 - \exp(-2\kappa a_2)]/\kappa a_2\} . \quad (21)$$

Using Derjaguin method, they obtain

$$V(H) = \pi a_1 a \rho_1 \rho_2/\varepsilon_r\varepsilon_0\kappa^4\cdot[e^{-\kappa H}/(a_1 + a_2)] . \quad (22)$$

If using the improved Derjaguin approximation, we obtain

$$V(H) = \pi a_1 a_2 \rho_1 \rho_2/\varepsilon_r\varepsilon_0\kappa^4\cdot e^{-\kappa H}/(a_1 + a_2)] \cdot[2\mathbf{a}/(2\mathbf{a} + H)] . \quad (23)$$

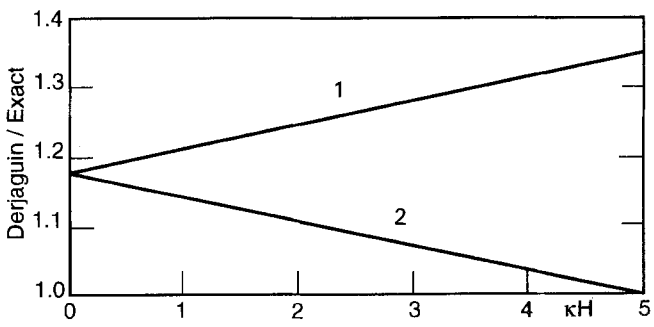
Figure 2 shows some exact results of calculation viz Eq. (21) for the interaction energy of two ion-penetrable spheres in comparison with those obtained with Eqs. (22) and (23). Figure 2 demonstrates that the accuracy of the improved Derjaguin approximation is better than that of classical Derjaguin method.

After 60 years, Papadopoulos et al. [11] first proposed a method for improvement of an old approximate assumption suggested by Derjaguin in 1934. The difference between the two approaches is that two interacting rings behave as two parallel ones, divided by a distance not equal to a straight-line segment, but equal to the arc of a circle, which is perpendicular to both rings. Their method has inherited the approximations introduced by Derjaguin and is expected to give good results for large κa and small κH. Their results are always higher than "exact" values at large κH, for example, at $\kappa a = 5$, $\kappa H = 4$ relative error is 18%, even though their method has further modification at small κa, the error is considerable. The proposed

Table 4 Comparison of present results Eq. (20) with the results of OCHW

	κH	$V_R/[4\pi\varepsilon\lvert\psi_1\psi_2\rvert a_1 a_2/(a_1 + a_2)]$ OCHW	Eq. (20)
	0.5	0.4069	0.4091
$\psi_1 = 2\psi_2$	1	0.2855	0.2844
$\kappa a_1 = 20$	2	0.1169	0.1159
$\kappa a_2 = 10$	3	0.0436	0.0434
	4	0.0157	0.0157
	0.5	−0.9584	−0.9719
$\psi_1 = -2\psi_2$	1	−0.4548	−0.4596
$\kappa a_1 = 20$	2	−0.1366	−0.1374
$\kappa a_2 = 10$	3	−0.0460	−0.0462
	4	−0.0160	−0.0161

Fig. 2 The ratio of 1) the classical Derjaguin approximation and 2) the improved Derjaguin approximation to the exact interaction free energy for two charged ion-penetrable spheres; $\kappa\ a_1 = 20$, $\kappa\ a_2 = 10$



method does not constitute an exact solution to the problem of colloidal interaction, therefore, the applicability of the method is limited.

The present method seems to be a bridge that links Derjaguin approximation with LSA, which gives consideration to both small and large particles separation, and to both small and large κa. We believe that the method has, to some extent, narrowed the theoretical gap between the above two limited cases. The accuracies of Eq. (12) and Eq. (20) are quite enough to meet computative needs, furthermore, because of its simple analytic form of formulas, it will be convenient for use. For the cases of high surface potential and constant surface charge, so long as high accurate formulas of two parallel plates exist, improved approximation has also good results.

Appendix

Consider the two equal spheres, having radius a, at separation $R = O_1,O_2$ between their centers O_1,O_2 (Fig. 1). Here,

$$b^2 = a^2 + R^2 - 2aR\cdot\cos\theta \tag{A1}$$

We may expect most of the contribution to the interaction free energy to come from the region where angle θ is small; this is very important for large particles at small separation. It is natural that angle θ is small at large separation. We therefore expand b, defined in (A1), in power of angle θ to obtain

$$b \approx R - a + aR\theta^2/2(R-a) = a + H + aR\theta^2/(a+H)\ . \tag{A2}$$

From Fig. 1,

$$h = a\cdot\sin\theta \approx a\theta\ , \tag{A3}$$

therefore,

$$b/(a+H) = 1 + hR\theta/2(a+H)^2\ . \tag{A4}$$

If κa is not very large, and κH is not very small, that is to say, $a \approx H$, we obtain

$$H\theta^2/2a \approx h^2/2a^2\ . \tag{A5}$$

Angle θ is less than unity, therefore

$$H/2a > h^2/2a^2\ ; \tag{A6}$$

let

$$\theta \approx (1 - 1/\kappa H)^{1/2}\ , \tag{A7}$$

thus,

$$\kappa H/2\kappa a - 1/2\kappa a \approx h^2/2a^2\ , \tag{A8}$$

and Eq. (6) is proved.

In the original Derjaguin's method, no matter whether small or large κH, angle θ must be very small, which ensures that the layers giving important contributions shall be practically parallel, the curvature of the surface beginning to be felt only where the contribution to the repulsive energy is negligible. In Eq. (A7) angle θ changes with the separation between the spheres. The curvature corrections are included; this is especially important for large particle separation. For small κH, it is not important.

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