ρ_p = density of the catalyst particle, kg/m^3
ρ_M = molar density of the solution, kmol/m^3
ϵ = catalyst particle porosity
τ = tortuosity factor of the catalyst

Subscripts

g = gas phase
gi = gas entering the reactor
go = gas leaving the reactor
l = liquid phase
s = external surface of the catalyst
$*$ = gas-liquid interphase

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Theory on Colloidal Double-Layer Interactions

The potential energy between two interacting colloidal particles is derived by a knowledge of the energy of interaction of two parallel flat plates. The proposed method maps pairs of infinitesimal surface elements from the two interacting bodies to parallel plate-like elements. The results obtained from this theory are compared with the Derjaquin approximation for large κR and the Levine and Dube approximation for small κR.

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SCOPE

An understanding of the forces acting between interacting particles in a colloidal suspension is essential for the explanation of the macroscopic phenomena of colloidal stability and coagulation. Controlled colloidal phenomena may in turn be used for the reclaiming of precious materials from wastes, water pollution control, and the production of numerous industrial and consumer goods.

In many instances the most important interparticle forces are those which arise from the interaction of the electrical double

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layers around the suspended particles. In 1934 Derjaguin saw that information for surface interaction between two spheres can be extracted from information for surface interaction between two planes which have the same surface as the spheres and are immersed in the same medium. For two interacting spherical colloids Derjaguin assumed that most of the surface interaction comes from the surface near the minimum distance of separation. Dividing the two spheres into infinitesimal rings facing each other, he also assumed that those rings were parallel, and by summing up their contributions he obtained the total interaction.

The assumption in Derjaguin's equation, that the infinitesimal rings are parallel, breaks down as the rings are removed from the minimum distance of separation. Furthermore, his assumption that most of the interaction comes from the area of spheres nearest to the minimum distance of separation, is valid only when the spheres interact at very short distances. Thus, predictions of surface energies of interaction based on Derjaguin's theory are good when the thickness of the double layer is small compared to the radii of the colloids and for short distances of separation. For interacting particles with much different size, Derjaguin's approach fails as well.

In this work two interacting spheres are divided into infinitesimal rings, perpendicular to the minimum distance of separation, as in Derjaguin's theory. The difference 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 ℓ, which is perpendicular to both rings. Thus, the interacting pair is mapped to a parallel pair of rings, separated by a distance ℓ. The same analysis for two-parallel cylindrical colloids uses the mapping of infinitesimal stripes from the two cylinders to parallel interaction stripes, separated again by a distance ℓ.

The proposed method does not constitute an exact solution to the problem of colloidal interactions. It represents an improvement of an old approximate theory which takes into account the lack of parallelism between interacting infinitesimal parts of the colloidal surfaces.

CONCLUSIONS AND SIGNIFICANCE

The predictions based on the presented approximation agree with predictions obtained from the Derjaguin equation for two interacting spheres and the Sparnaay equation (1959) for two interacting cylinders, for large κR where Derjaguin's assumptions are valid. For small κR, our results are in general agreement with those of Levine and Dube (1939). Hence, where Derjaguin's assumptions are no longer satisfactory, our method provides substantial improvements in predicting colloidal interactions. It should be noted that since 1934 there has not been another approach to obtaining spherical interactions from planar ones. Even more recent studies of colloidal interactions

(Ohshima, Healy and White, 1982) use Derjaguin's equation without further modification. In this paper we concentrate on the case of double-layer interactions between spheres and cylinders of equal size and the same type of surface.

Another attractive feature of this theory is that it may be extended to predict interactions of colloidal particles with arbitrary shape. This may be realized by connecting parts of infinitesimal elements of two interacting colloids with circular arcs perpendicular to the surface elements and by subsequently mapping the latter to parallel ones.

INTRODUCTION

The potential energy of interaction between two interacting colloids in a suspension affects greatly the rate of its coagulation. This is seen in the stability ratio W, defined by Fuchs in 1934 as ν_o/ν, where ν_o is the velocity of coagulation in a sol without particle interactions and ν the rate of coagulation in a sol where interactions exist. This theory assumes that when two particles meet they unite to form a new particle. W as derived by Fuchs is given by

$$W = 2R \int_{2R}^{\infty} \frac{\exp(V(x)/kT)}{x^2} dx \qquad (1)$$

where $V(x)$ is the energy between two colloids of radius R. When the interacting particles approach each other at very close distances, there is a decrease in their composite diffusion coefficient. Accordingly, Derjaguin and Müller (1967) modified the stability ratio as

$$W = 2R \int_{2R}^{\infty} \frac{D(\infty)}{D(x)} \frac{\exp(V(x)/kT)}{x^2} dx \qquad (2)$$

in which $D(\infty)$ and $D(x)$ are the diffusion coefficients at large separations and at small separations x, respectively.

Based on a hydrodynamic analysis presented by Brenner (1961), Honig et al. (1971) gave an expression for the ratio of these coefficients:

$$\frac{D(\infty)}{D(x)} = \frac{1 + (13R/6x) + (R^2/3x^2)}{1 + 2R/3x} \qquad (3)$$

Equations 1 and 2 show that knowledge of $V(x)$ is very important in predicting colloidal stability. Moreover, if $V(x)$ can be varied in a desirable manner, the stability of a suspension may then be controlled.

The energy of interaction $V(x)$ comes from electrical, van der Waals, chemical and steric contributions. The electrical forces arising from the overlapping of the double layers of the interacting particles are the most important in the absence of polyelectrolytes and chemical complexes.

The surface of a suspended solid in a liquid medium usually chemisorbs some types of ions, thus, creating a deficit of these ions in the bulk of the solution. At the same time ions with opposite charges are in excess in the bulk, so that the net charge on the surface of the particles is counterbalanced by an opposite net charge in the bulk of the solution. The closest layer of charge to the particles' surface is fairly two-dimensional, while further from the surface the distribution of opposite charges is diffuse and three-dimensional. The whole region constitutes the electrical double layer.

The free energy of interaction of two colloids, as a result of the overlapping of their electrical double layers, is

$$G = G(H_O) - G_1 - G_2 \qquad (4)$$

Here $G(H_O)$ is the free energy of the two-particle system at a separation distance H_O, and G_1 and G_2 the free energies of the colloids when they do not interact. The free energy of a double-layer system is in turn given (Verwey and Overbeek, 1948) as
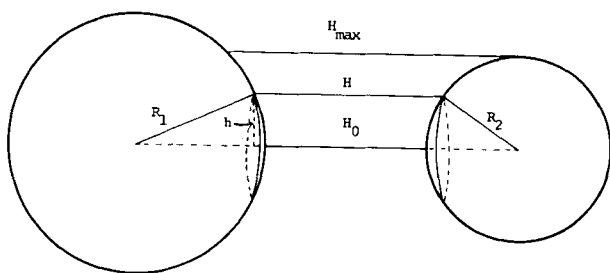
Figure 1. Representation of the interaction of circular rings in Derjaguin's theory.

$$G = \int_0^1 \frac{d\xi}{\xi} \int \int_{-\infty}^\infty \int \psi'(x,y,z)\rho'(x,y,z)dxdydz \quad (5)$$

where ξ is the degree of charging of ions in the double-layer, ψ' is the electrical potential of a point in space, and ρ' the charge density. ψ' may be obtained from the Poisson-Boltzmann equation,

$$\nabla^2\psi = \frac{8\pi nez}{D}\sinh\frac{ze\psi}{\kappa T} \quad (6)$$

Here z is the valency of a $z{:}z$ electrolyte, n the ionic concentration, e the charge of an electron, D the medium's dielectric constant, T the temperature, and ψ the electrical potential. For sufficiently small ψ the Debye-Hückel assumption

$$\sinh\frac{ze\psi}{\kappa T} \simeq \frac{ze\psi}{\kappa T}$$

may be used so that

$$\nabla^2\psi = \kappa^2\psi \quad (7)$$

where

$$\kappa^2 = \frac{8\pi ne^2z^2}{DkT} \quad (8)$$

In 1932 Bradley suggested that van der Waals forces are important in particle interactions due to the fact that each atom in one particle attracts every atom in the other particle. The correct expression for the van der Waals attraction between two spheres was derived by Hamaker in 1937 and is referred to as "body" or Hamaker interaction. If H_O is the minimum separation distance between two spheres, R_1 and R_2 the radii, and if we define $x = H_O/2R_1$ and $y = R_2/R_1$, the Hamaker expression for the energy of interaction is

$$E = \frac{A}{12}\left\{\frac{y}{x^2 + xy + x} + \frac{y}{x^2 + xy + x + y}\right.$$
$$\left. + 2ln\frac{x^2 + xy + x}{x^2 + xy + x + y}\right\} \quad (9)$$

In the same work Hamaker also derived the equation for body interactions per unit area between two semi-infinite slabs separated by a distance x as

$$E = \frac{A}{12\pi x^2} \quad (10)$$

This equation is very useful for the experimental determination of the value of A, known as Hamaker's constant. This is done by immersing two well-polished surfaces in a liquid, parallel at a distance x, and subsequently measuring the force of attraction with a very sensitive balance (Derjaguin et al., 1954).

The chemical and steric forces are caused by specific adsorption of large polymeric molecules and/or complexes which affect coagulation not simply through modification of the surface charge on the particles, but rather through interbridging action and steric hindrance.

In many instances, the most important interparticle forces are those which arise from the interaction of the electrical double layers around the suspended particles. The topic of double-layer interaction has consequently received most of the attention in the literature of colloidal stability. In dealing with the Poisson-Boltzmann equation, it is readily noticed that it may be solved relatively easily
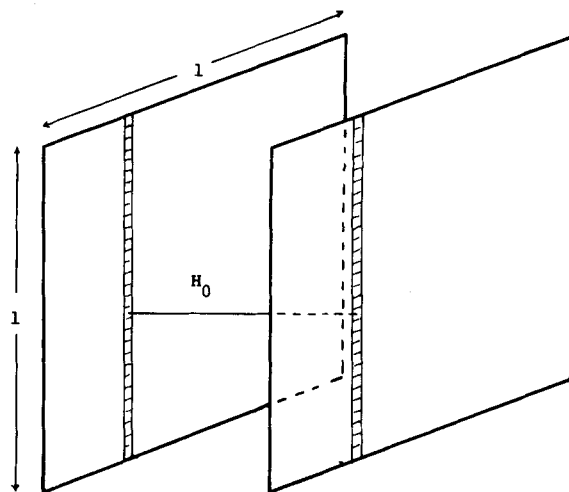

Figure 2. The interaction between two parallel planes of unit area.

for the case of two flat interacting double layers. In 1934, Derjaguin saw that information for surface interaction between two spheres can be extracted from information for surface interaction between two planes which have the same surfaces as the spheres and are immersed in the same medium. In this work the limitations of Derjaguin's theory are pointed out and a new theory is developed which carries fewer assumptions. Yet, Derjaguin's idea of mapping spherical surface interactions to planar ones is still used.

THEORY

For two interacting spherical colloids (Figure 1), Derjaguin assumed that most of the surface interaction comes from the surface near the minimum distance of separation H_O. Thus, by dividing the two spheres into infinitesimal rings facing each other, he assumed that those rings were parallel, and by summing up their contributions he obtained the total interaction. If the distance between two infinitesimal rings is H, then for the two spheres shown in Figure 1 we have

$$H = H_O + R_1 + R_2 - \sqrt{R_1^2 - h^2} - \sqrt{R_2^2 - h^2} \quad (11)$$

where h is the radius of the rings.

Differentiation of Eq. 11 gives us

$$\frac{dH}{dh} = \frac{h}{R_1\sqrt{1 - h^2/R_1^2}} + \frac{h}{R_2\sqrt{1 - h^2/R_2^2}} \quad (12)$$

which for $R_1, R_2 \gg h$ becomes

$$dH = \left[\frac{R_1 + R_2}{R_1R_2}\right]hdh \quad (13)$$

If $U(H)$ is the energy per unit area between two infinite parallel planes, and $V(H_O)$ the one between two spheres, the two are related by

$$V(H_O) = \int_0^{min(R_1,R_2)} U(H)2\pi hdh \quad (14)$$

and by making use of Eq. 13

$$V(H_O) = 2\pi\frac{R_1R_2}{R_1 + R_2}\int_{H_0}^\infty U(H)dH \quad (15)$$

The upper limit of the integral in Eq. 15 is taken as ∞ instead of H_{max} because for large values of H, $U(H) \to 0$.

At first sight it may be argued that Derjaguin's summation of pair interactions should include contributions from cross interactions, i.e., each infinitesimal ring on one sphere should interact with all infinitesimal rings on the other sphere. However, this is not the case since $U(H)$ is the surface energy of interaction between two infinite parallel planes, in which such cross interactions have already been taken into account. This may also be seen by observing
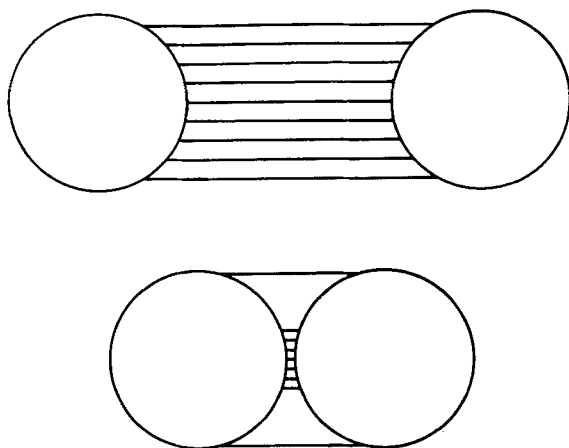
Figure 3. Interacting spheres at close and distant separations. Straight lines indicate distances between circular rings.
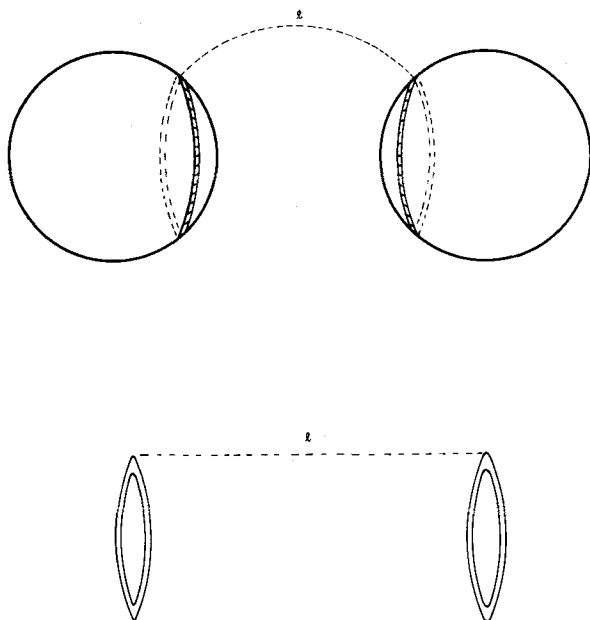

Figure 4. The mapping of a pair of interacting infinitesimal rings.

Figure 5. Lines of force for oppositively charged (a) and similarly charged (b) spheres.

Figure 6. Geometrical representation of two spherical colloids of equal radius R.
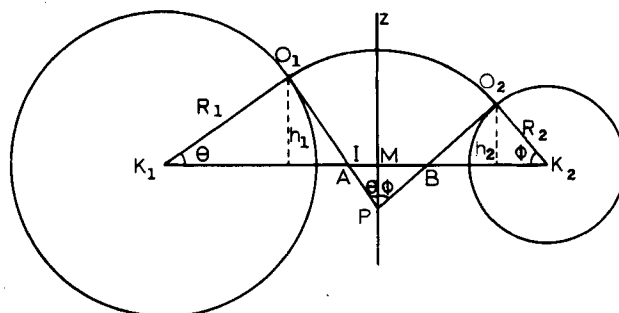
Figure 7. Geometrical representation of two spherical colloids of radii R_1 and R_2.

the interaction between two parallel planes of unit area, Figure 2. The summation of the surface energies of interaction between infinitesimal parallel elements separated by a distance H_O is

$$V(H_O) = \int_0^1 \int_0^1 U(H_O)dxdy = U(H_O) \qquad (16)$$

The assumption of Derjaguin's equation, that the infinitesimal rings are parallel, breaks down as the radii of the interacting rings increase. Besides, his assumption that most of the interaction comes from the area of spheres nearest to the minimum distance of separation is valid only when the spheres interact at very short distances, Figure 3. In other words, Derjaguin's approximation was suggested for separation distances smaller than the radii of the interacting particles, and is expected to offer relatively accurate predictions for large κR. Numerical calculations by Hoskin and Levine (1956) and recently by Ledbetter et al. (1981) verified the Derjaguin approach for large κR.

The approximation presented in this work is applicable to surface interactions such as the ones arising from the overlapping of the electrical double layers. The two interacting spheres are divided into infinitesimal rings, perpendicular to the minimum distance of separation, as in Derjaguin's theory. The difference between the two approaches is that two interacting rings behave as parallel,
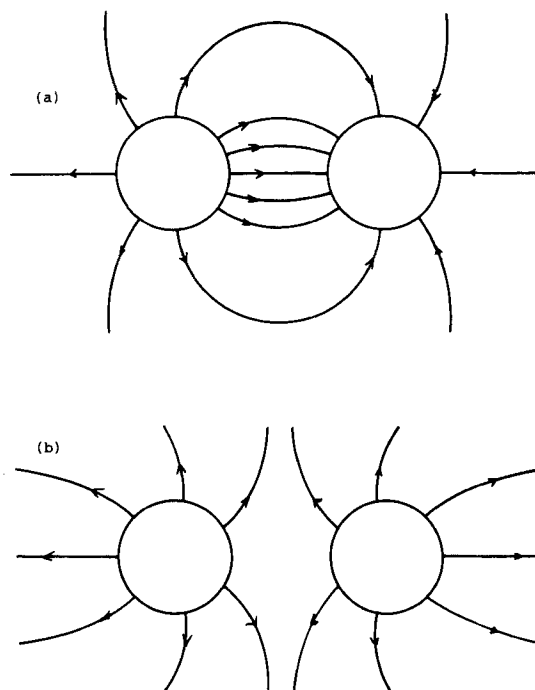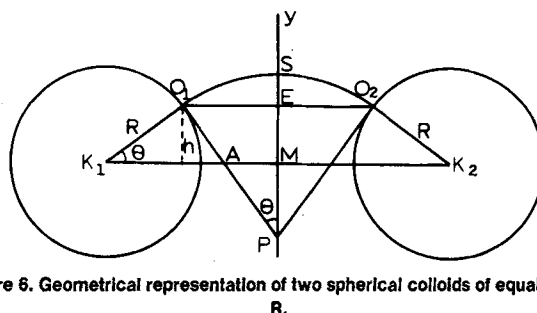
divided by a distance not equal to H (Figure 4) but equal to the arc of a circle which is perpendicular to both rings. Thus, the interacting pair is mapped to a parallel pair of infinitesimal elements, Figure 4. There is a unique infinite set of arcs that connect each point of one sphere to a point on the other sphere. These arcs are reminiscent of the lines of force of two spheres with opposite charge, Figure 5. It is also assumed that the main contribution comes from the interaction of the parts of the spheres that "face" each other, defined by the set of common outer tangent lines. Calculations verified the validity of this assumption.

By using geometrical arguments, it is found that for two spheres

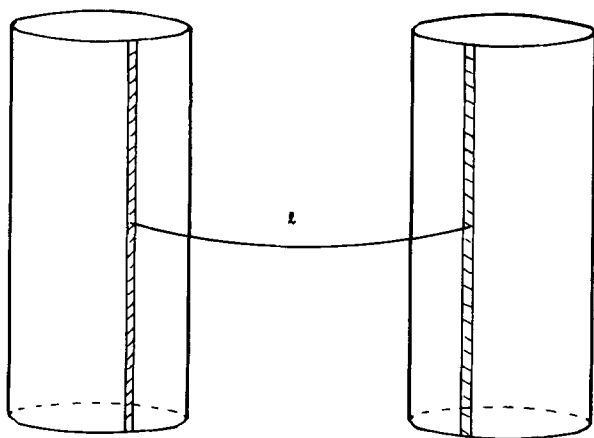**Figure 8. Two parallel cylindrical colloids and the interaction of infinitesimal stripes.**

of radius R as shown in Figure 6, the arc length of a circle, which is perpendicular to both spheres, is

$$\ell = O_1 O_2 = \frac{\theta}{\sin\theta}[H_O + 2R(1 - \cos\theta)] \qquad (17)$$

If the two interacting spheres in Figure 7 possess radii R_1 and R_2, ℓ is given by

$$\ell = \frac{\theta + \phi}{2\sin\theta}\left[2R_1\frac{\sin^2\theta}{\cos\theta} + d + \frac{R_1^2 - R_2^2}{d} - \frac{2R_1}{\cos\theta}\right] \qquad (18)$$

In Eq. 18, d is the distance between the centers of the spheres and ϕ is found as a function of θ.

A complete geometrical proof is found in the Appendix. In Figure 7, the radii of the interacting rings are h_1 and h_2 and the respective thicknesses $2\pi h_1 dh_1/\cos\theta$ and $2\pi h_2 dh_2/\cos\phi$. If we express h_1, h_2, dh_1 and dh_2 in terms of R_1, R_2, θ, and ϕ: $h_1 = R_1 \sin\theta$, $h_2 = R_2 \sin\phi$, $dh_1 = R_1 \cos\theta d\theta$, and $dh_2 = R_2 \cos\phi d\phi$, we are ready to get the total surface energy of interaction as

$$V(H_O) = \pi R_1^2 \int_0^{\theta_{max}} U(\ell)\sin\theta d\theta + \pi R_2^2 \int_0^{\theta_{max}} U(\ell)\sin\phi d\phi \qquad (19)$$

θ_{max} and ϕ_{max} are defined by $\theta_{max} + \phi_{max} = \pi$, and $U(\ell)$ is the energy of interaction per unit area of two parallel plates separated by a distance l. For two equal spheres Eq. 19 reduces to

$$V(H_O) = 2\pi R^2 \int_0^{\pi/2} U(\ell)\sin\theta d\theta \qquad (20)$$

It should be pointed out that in the case of unequal spheres, two interacting rings do not have the same radius and as a result they have unequal size. This case will be treated in a future paper.

A similar analysis for two parallel cylindrical colloids uses the mapping of infinitesimal stripes from the two cylinders to parallel interacting stripes, separated again by a distance ℓ, Figure 8. If the length of the colloids is L, the total energy of interaction is

$$V(H_O) = LR_1 \int_0^{\theta_{max}} U(\ell)d\theta + LR_2 \int_0^{max} U(\ell)d\phi \qquad (21)$$

and for cylinders of the same radius

$$V(H_O) = 2LR \int_0^{\pi/2} U(\ell)d\theta \qquad (22)$$

RESULTS AND DISCUSSION

The potential energy of repulsion between two similar, parallel, flat double layers is derived (Verwey and Overbeek, 1948) as

$$U^*(\kappa H) = \frac{U(H)}{D\kappa\psi_0^2} = \frac{1}{4\pi}\left(1 - \tanh\frac{\kappa H}{2}\right) \qquad (23)$$

TABLE 1. DOUBLE LAYER ENERGY OF INTERACTION BETWEEN TWO SPHERICAL COLLOIDS BY THE TWO METHODS

κR	κH_O	V^*_{sph}[a]	V^*_{sph}[b]	% Difference
0.5	0.5	0.1148	0.2370	51.6
	1.0	0.0724	0.1566	53.8
	2.0	0.0261	0.0635	58.8
	4.0	0.00297	0.00907	67.3
	6.0	3.33×10^{-4}	0.00124	73.1
	8.0	3.82×10^{-5}	1.68×10^{-4}	80.3
	10.0	4.48×10^{-6}	2.27×10^{-5}	82.6
4.0	0.5	0.2128	0.2370	10.2
	1.0	0.1385	0.1566	11.6
	2.0	0.0543	0.0635	14.5
	4.0	0.0073	0.0091	20.1
	6.0	9.27×10	0.00124	25.1
	8.0	1.18×10^{-4}	1.68×10^{-4}	29.6
	10.0	1.51×10^{-5}	2.27×10^{-5}	33.5
10.0	0.5	0.2267	0.2370	4.4
	1.0	0.1488	0.1566	5.0
	2.0	0.0594	0.0635	6.3
	4.0	0.00825	0.00907	9.1
	6.0	0.00109	0.00124	11.8
	8.0	1.44×10^{-4}	1.68×10^{-4}	14.3
	10.0	1.89×10^{-5}	2.27×10^{-5}	16.7
24.0	0.5	0.2326	0.2370	1.9
	1.0	0.1533	0.1566	2.1
	2.0	0.0617	0.0635	2.7
	4.0	0.00871	0.00907	4.0
	6.0	0.00117	0.00124	5.3
	8.0	1.57×10^{-4}	1.68×10^{-4}	6.5
	10.0	2.10×10^{-5}	2.27×10^{-5}	7.7

[a] This work.
[b] Eq. 25.

Here, $U^*(\kappa H)$ is the dimensionless energy of interaction between two plates separated by a distance H. This derivation is based on the assumption that the surface possesses a potential ψ_0 small enough for the Debye-Hückel assumption to hold. The Derjaguin equation for two spheres of the same radius R may be written as

$$V(H_O) = \pi R \int_{H_O}^{\infty} U(H)dH \qquad (24)$$

Use of Eq. 23 in Eq. 24 will give the dimensionless energy of repulsion between two spherical colloids of radius R as:

$$V^*_{sph}(\kappa H_O) = \frac{V_{sph}(H_O)}{DR\psi_0^2} = \frac{1}{2}ln(1 + e^{-\kappa H_0}) \qquad (25)$$

This equation inherits the approximations introduced by Derjaguin and is expected to give good results for certain ranges of the minimum distance of separation H_O and the inverse of the thickness of the double layer κ, namely for large κR and small κH_O. It also shows that $V_{sph}(H_O)$ varies linearly with R. The limitations of Eq. 25 have also been discussed by Verwey and Overbeek (1948).

In this study, Eq. 23 is used in Eq. 20 for the calculation of $V^*_{sph}(\kappa H_O)$ for a wide range of κR and κH_O. The results are shown in Table 1 and are compared with the results obtained from the use of Eq. 25. As expected, Derjaguin's theory gives higher values for $V^*_{sph}(\kappa H_O)$ than our method does. The two approaches give almost identical results for the ranges of κR and κH_O in which Derjaguin's assumptions are valid. Although the relative difference increases with κH_O, the absolute difference becomes less pronounced due to the fact that the energy decreases with increasing κH_O.

For small κR our results were compared with the approximation of Levine and Dube (1939), which was derived for small κR. This method gives the dimensionless energy for constant surface potential as

$$V^* = \frac{e^{-\kappa H_O}}{s}\beta \qquad (26)$$

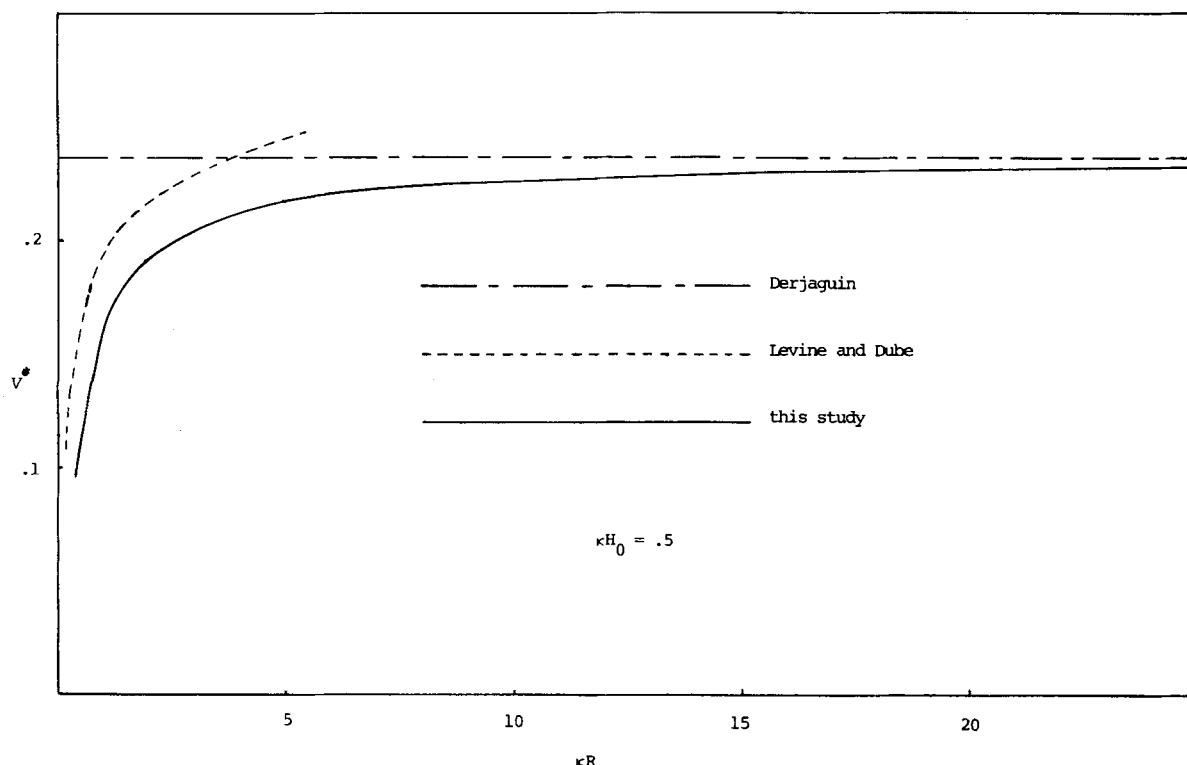where $s = (H_O + 2R)/R$ and β is a function of κH_O, κR and s. The

Figure 9. The dimensionless double-layer energy of interaction as a function of the dimensionless particle radius κR, for constant dimensionless distance of separation $\kappa H_O = .05$.

value of β lies between 0.6 and 1.0 and is tabulated in the book of Verwey and Overbeek (1948). In Figures 9, 10 and 11 we show the behavior of V^* based on Derjaguin's, Levine and Dube's and our approximations. V^* is plotted against κR for three typical values of the dimensionless distance of separation κH_O. In these figures we see that the prediction based on Derjaguin is constant with κR, which implies a linear dependence of the dimensional energy V

on R. In Figure 9 ($\kappa H_O = 0.5$), for some small values of κR (i.e., $\kappa R = 2, 3, 4$), V^* based on Levine and Dube becomes sufficiently larger than is V^* based on Derjaguin's approximation. This happens at a κR range where already Derjaguin's approximation overestimates the actual interaction by significant amount. At extremely small κR Levine and Dube's and our results are in agreement for $H_O = 0.5$. For $H_O = 2.0$ our results agree with Levine and Dube's

Figure 10. The dimensionless double-layer energy of interaction as a function of the dimensionless particle radius κR, for constant dimensionless distance of separation $\kappa H_O = 2$.
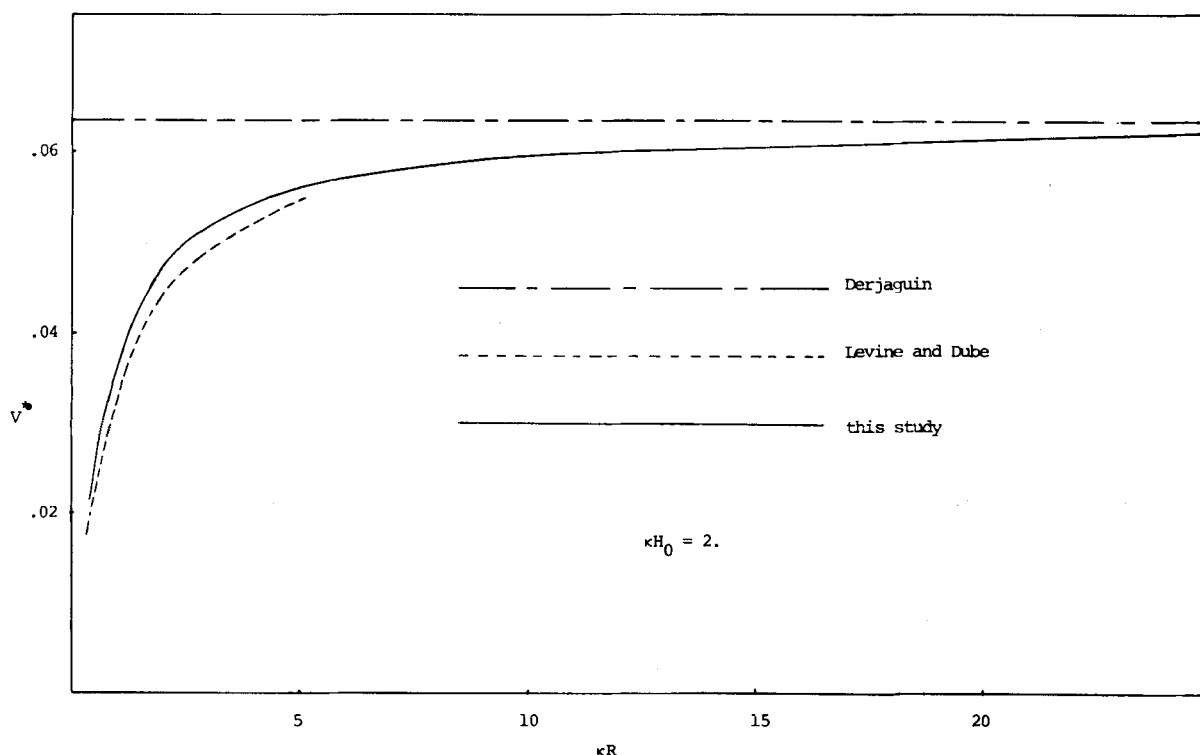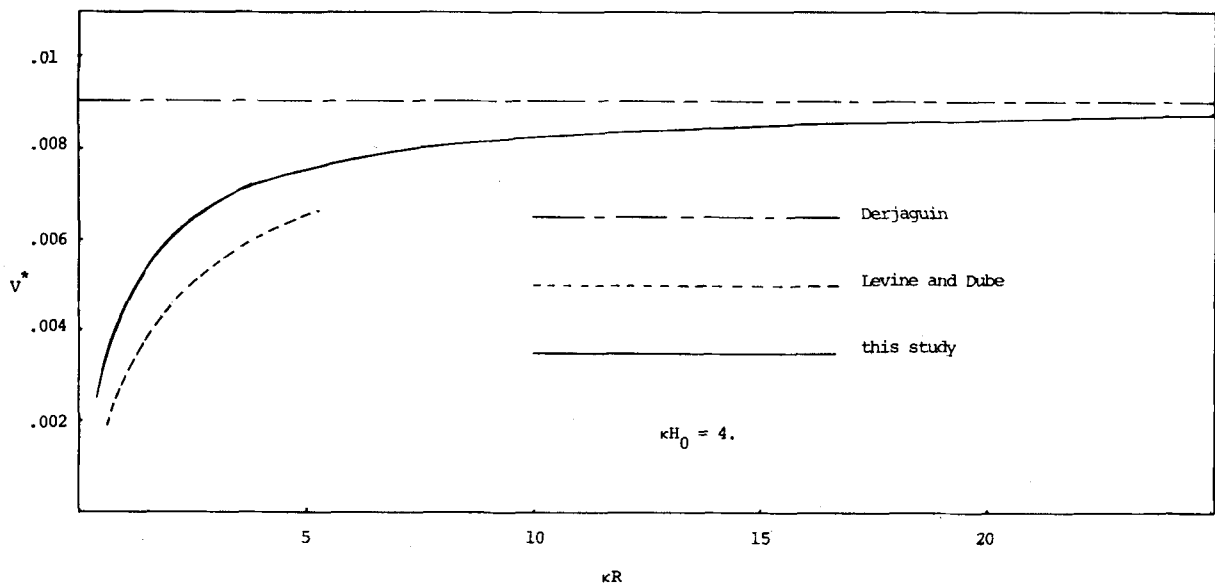
Figure 11. The dimensionless double-layer energy of interaction as a function of the dimensionless particle radius κR, for constant dimensionless distance of separation $\kappa H_O = 4$.

TABLE 2. DOUBLE LAYER ENERGY OF INTERACTION BETWEEN TWO PARALLEL CYLINDRICAL COLLOIDS CALCULATED BY THE TWO METHODS

κR	κH_O	V^*_{cyl}[a]	V^*_{cyl}[b]	% Difference
0.5	0.5	0.1349	0.1711	21.2
	1.0	0.0889	0.1173	24.2
	2.0	0.0347	0.0493	29.7
	4.0	0.00442	0.00721	38.7
	6.0	5.41×10^{-4}	9.87×10^{-4}	45.2
	8.0	6.68×10^{-5}	1.34×10^{-4}	50.1
	10.0	8.36×10^{-6}	1.81×10^{-5}	53.8
4.0	0.5	0.0588	0.0605	2.8
	1.0	0.0397	0.0415	4.2
	2.0	0.0164	0.0174	5.9
	4.0	0.00231	0.00255	9.3
	6.0	3.06×10^{-4}	3.49×10^{-4}	12.3
	8.0	4.02×10^{-5}	4.73×10^{-5}	15.1
	10.0	5.28×10^{-6}	6.40×10^{-6}	17.6
10.0	0.5	0.0377	0.0383	1.4
	1.0	0.0256	0.0262	2.3
	2.0	0.0107	0.0110	3.1
	4.0	0.00154	0.00161	4.7
	6.0	2.07×10^{-4}	2.20×10^{-4}	6.1
	8.0	2.77×10^{-5}	2.99×10^{-5}	7.5
	10.0	3.69×10^{-6}	4.05×10^{-6}	8.9
24.0	0.5	0.0244	0.0247	1.2
	1.0	0.0166	0.0169	1.9
	2.0	0.00695	0.00712	2.3
	4.0	0.00101	0.00104	3.0
	6.0	1.37×10^{-4}	1.42×10^{-4}	3.7
	8.0	1.85×10^{-5}	1.93×10^{-5}	4.3
	10.0	2.48×10^{-6}	2.61×10^{-6}	5.0

[a] This work.
[b] Eq. 27.

for a significant range of small κR. For $\kappa H_O = 4.0$ our method predicts larger values for V^* than those based on Levine and Dube's equation.

In 1959 Sparnaay used Derjaguin's approach for the study of the double layer interaction between two parallel cylindrical colloids, and the dimensionless potential energy of the system was found to be

$$V^*_{cyl}(\kappa H_O) = \frac{V_{cyl}(H_O)}{DR\psi_0^2 \kappa L} = \frac{1}{2\sqrt{\pi \kappa R}} \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{n} e^{-n\kappa H_0} \quad (27)$$

This equation possesses the same parameter range of validity as Eq.

25 since both were derived on the basis of the same assumptions. The present method uses Eq. 23 in Eq. 22 for the calculation of $V^*_{cyl}(\kappa H_O)$. As it may be seen from Table 2, the results of this theory are satisfactory for the case of two parallel interacting cylinders. The predictions are in good agreement with Sparnaay's equation within the validity range of the latter. Outside this range, the energy of interaction based on the presented method shows a deviation from Sparnaay's development that has the correct sign.

NOTATION

A	= Hamaker constant
D	= dielectric constant
$D(x)$	= composite diffusion coefficient
E	= colloidal van der Waals energy of interaction
G	= free energy
H	= distance between two interacting rings
H_O	= minimum distance of separation
L	= length of a cylindrical colloid
R, R_1, R_2	= radii of spherical and cylindrical colloids
T	= temperature
$U(H)$	= energy of interaction per unit area between two parallel flat double layers
$U^*(\kappa H)$	= dimensionless $U(H)$
$V(x)$	= total potential energy of interaction between two colloids
$V(H_O)$	= double layer energy of interaction between two colloids
$V^*_{cyl}(\kappa H_O)$	= dimensionless $V(H_O)$ for two cylinders
$V^*_{sph}(\kappa H_O)$	= dimensionless $V(H_O)$ for two spheres
∇	= del operator
d	= distance beween the centers of two colloids
e	= charge of an electron
h, h_1, h_2	= radii of interacting rings
k	= Boltzmann constant
ℓ	= length of arc which connects pair of infinitesimal rings
n	= ionic concentration
z	= valency of ions in symmetrical electrolyte

Greek Letters

Δ	= difference
θ, ϕ	= angles
κ	= inverse of the Debye length

ν = rate of coagulation
ξ = degree of charging of double layer
ρ = charge density
ψ = electric potential

APPENDIX

In Figure 6 we denote by d and the line segment K_1K_2 and draw a line y perpendicular to K_1K_2 at its middle. Radius R in circle (K_1, R) forms an angle θ with K_1K_2 and cuts the circumference at point O_1. If a line is drawn perpendicular to R at O_1, it cuts y at P. Due to symmetry, O_1P is the radius of the circle which cuts normally both (K_1, R) and (K_2, R). Thus, $O_1P = O_2P$, $O_2K_2K_1 = \theta$, and $O_1PO_2 = 2\theta$. Then the arc length $\ell = O_2O_2 = 2\theta \cdot O_1P$. Use of $O_1P = O_1E/\sin\theta$ and $O_1E = 1/2(H_O + 2R(1 - \cos\theta))$ leads to Eq. 17:

$$\ell = O_1O_2 = \frac{\theta}{\sin\theta}\{H_O + 2R(1 - \cos\theta)\} \tag{A1}$$

The limiting values of O_1O_2 are

$$\lim_{\theta \to 0} O_1O_2 = H_O \quad \lim_{\theta \to \pi/2} O_1O_2 = (H_O + 2R)\pi \tag{A2}$$

When the two circles possess different radii use is made of a geometrical theorem according to which the locus of all points that are centers of circles which cut normally (K_1, R) and (K_2, R) is a straight line z perpendicular to K_1K_2 (Figure 7). If M is the point where z cuts K_1K_2 and I the middle of d, the length of IM is

$$IM = \frac{R_1^2 - R_2^2}{2d} \tag{A3}$$

for $R_1 > R_2$. The circle with center P which cuts normally (K_1, R) and (K_2, R) has radius $O_1P = O_2P$ and depends on θ, d, R_1, and R_2. Observing that $O_1P = O_1A + AP$, $O_1A = R_1 \tan\theta$ and $AP = AM/\sin\theta$, O_1P may be easily obtained

$$O_1P = \frac{1}{2\sin\theta}\left(2R_1\frac{\sin^2\theta}{\cos\theta} + d + \frac{R_1^2 - R_2^2}{d} - \frac{2R_1}{\cos\theta}\right) \tag{A4}$$

The angle which corresponds to O_1O_2 is $O_1PO_2 = \theta + \phi$. In order to express ϕ in terms of θ, we need to observe that $MB/MP = \tan\phi$ from which it follows that

$$\frac{\dfrac{d}{2} - \dfrac{R_1^2 - R_2^2}{2d} - \dfrac{R_2}{\cos\phi}}{\dfrac{d}{2} + \dfrac{R_1^2 - R_2^2}{2d} - \dfrac{R_1}{\cos\theta}} = \frac{\tan\phi}{\tan\theta} \tag{A5}$$

Finally, the arc length l is readily obtained as expressed in Eq. 18, which simplifies to Eq. 17 for $R_1 = R_2 = R$.

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