PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

The Interaction of Two Identical Spherical Colloidal Particles. I. Potential Distribution

N. E. Hoskin

Phil. Trans. R. Soc. Lond. A 1956 **248**, 433-448
doi: 10.1098/rsta.1956.0004

THE INTERACTION OF TWO IDENTICAL SPHERICAL COLLOIDAL PARTICLES

I. POTENTIAL DISTRIBUTION

By N. E. HOSKIN†

Computing Machine Laboratory, University of Manchester

(*Communicated by G. Gee, F.R.S.—Received* 12 *April* 1955)

CONTENTS

The potential distribution in the electric double layers of two identical spherical colloidal particles is obtained numerically for cases covering wide ranges of the particle radius, particle separation and surface potential. The method of solution of the Poisson–Boltzmann equation by finite differences on an electronic computer is described, and the distributions obtained are used to discuss the accuracy of the approximate methods that have been developed. It is shown that a series of spherical harmonics (which is only valid for low surface potential) is practical only for small particles and large separation, and unless these conditions hold, accurate results may only be obtained by retaining many terms in the series.

1. Introduction

The solutions to a number of problems in the theory of hydrophobic colloidal systems require the evaluation of the forces acting between the colloidal particles, the most important problem, and indeed the one which can receive immediate consideration, being the determination of the conditions which govern stability. Others are the dependence on sol concentration of such transport phenomena as diffusion, viscosity, rate of sedimentation and electrophoresis. Practically all the theoretical work on the dependence on sol concentration of these properties has dealt with the hydrodynamical interaction between the colloidal particles. It is clear, however, that the repulsion between the electric double layers of the particles must play a role, particularly at low electrolyte concentrations when the repulsion is of a long-range character. Recently, some attention has been given to the effect of the electrical forces between the particles on viscosity (Harmsen, Schooten & Overbeek 1953) and electrophoresis (Stigter 1954). However, at present, there are no mathematical theories which treat these phenomena, so that it cannot be claimed that a detailed quantitative application of any calculations of the forces between colloidal particles is an immediate possibility. Nevertheless, there is little doubt that an adequate theory of the dependence

† Present address: Atomic Weapons Research Establishment, Berkshire.

on concentration of the various transport phenomena mentioned above will require a knowledge of these forces.

There are two contributions to the force between the colloidal particles, namely, the van der Waals–London attraction and the electric repulsion of the double layers. Although there is still uncertainty concerning the value of the constant in the expression for the London attraction and although this expression becomes more complicated at large separation as a result of the retardation effect, it is perhaps true to say that the repulsive force is the more difficult to determine. This difficulty arises mainly because it is necessary to solve the non-linear Poisson–Boltzmann (P.B.) equation in order to find the distribution of the electric potential in the overlapping double layers of the particles.

If the particles be regarded as sections of parallel plates of infinite area (so that the problem becomes one-dimensional) then an analytical solution of the P.B. equation can be found, although it may have to be expressed in terms of hyperelliptic integrals when there are trivalent ions (or ions of higher valency) present in the electrolyte. The problem for a binary symmetrical electrolyte was first considered by Langmuir (1938); systems of higher valency types have been considered by Robinson & Wood (1946) and others. However, this model is obviously not as useful as that of two spherical particles, since in many colloidal systems the particles can be assumed to be almost spherical. Unfortunately, the mathematical problem is now much more difficult, and no analytical solution which is applicable for all ranges of the parameters involved has yet been found. Because of the difficulty of finding the potential distribution analytically it was decided to obtain solutions by a purely numerical method. This demanded a large amount of computation which was carried out on the Manchester University Electronic Computer, without which the problem would have been impracticable.

The immediate application of these solutions is in the determination of the repulsive force between two spherical particles and this is discussed in the following part II (Hoskin & Levine 1955). However, there may well be other applications of these solutions. For example, Morris (1952) has obtained some experimental results on the dependence of surface conductivity on sol concentration. A theoretical interpretation of these results will require a knowledge of the potential distribution in the interacting double layers of spherical particles. Furthermore, the above-mentioned numerical solutions will certainly be helpful in suggesting the form of solution and in establishing the accuracy in any theoretical investigation of the potential that may be attempted in the future. An important result of the numerical computation is that, except possibly when the 'thickness' of the diffuse layer $(1/\kappa)$ is greater than the particle radius, the effect of interaction is confined to the region lying between the two spheres. Consequently the potential distribution on the 'outer' sides is almost the same as that for a single sphere.

2. The Poisson–Boltzmann equation

The following discussion only considers the case of a binary symmetrical electrolyte, and it is assumed that the potential ψ in the double layer surrounding two spherical particles of radius a and separation R satisfies the equation

$$\nabla^2\psi = \frac{8\pi nez}{\epsilon}\sinh\frac{ze\psi}{kT}, \qquad (2{\cdot}1)$$

where ϵ = dielectric constant of the solution,

n = no. of positive (or negative) ions per cm^3 at infinity,

e = elementary charge of each ion,

z = valency of either type of ion,

k = Boltzmann's constant,

T = absolute temperature.

Equation (2·1) may be rewritten as

$$\nabla'^2\phi = \sinh\phi \tag{2·2}$$

by means of the substitutions

$$\phi = ze\psi/kT, \quad \kappa^2 = 8\pi ne^2z^2/\epsilon kT. \tag{2·3}$$

The dash in the Laplacian operator signifies that co-ordinates are measured in units of $1/\kappa$, and henceforth in this paper, unless otherwise stated, all distances will be in these units and will be denoted by a dash with the exception of two new symbols which we now introduce, namely $\tau = \kappa a$ and $s = R/a = R'/\tau$.

The potential ψ vanishes at an infinitely large distance from the particles and therefore ϕ will also tend to zero at infinite distance. If the ions constituting the surface charge are identical with one of the lattice ions of the colloidal particles, and also if there is either no absorption of counter-ions or no 'intrinsic' charge, then the potential is constant over the whole particle surface and is independent of the separation of the particles, depending only on the type and concentration of electrolyte. This case occurs frequently, and even if there is specific absorption there is theoretical evidence (Verwey & Overbeek 1948; Levine 1951) that the surface potential is still approximately uniform provided the separation is not too small; therefore the remaining boundary condition chosen is that of constant potential (i.e. ϕ = constant = Φ, say, in (2·2)) on the particle surfaces.

Equation (2·2) is difficult to solve, because of its non-linearity, and much of the theoretical discussion has been confined to the approximate equation of Debye & Hückel (1923, 1924), who for their theory of strong electrolytes replaced (2·2) by

$$\nabla'^2\phi = \phi. \tag{2·4}$$

However, this substitution is valid only if ϕ is small, and for larger values accurate solutions to (2·2) must be obtained numerically. This has been done for a single spherical particle by Muller (1928) for fairly low values of the radius and potential and by Hoskin (1953) for wider ranges of these parameters. Comparisons between the accurate solutions and those obtained from (2·4) show that (2·4) may only be used with safety if $\phi < 1$ or if $\tau < 1$. Levine & Dube (1940) used equation (2·4) to obtain a solution for the case of two equal spheres in the form of an infinite series of which they obtained explicitly the first three terms, while Derjaguin (1940) extended his treatment of infinite parallel plates to the case of two spheres of large radius, considering them as being composed of a series of parallel circular rings. This method will be discussed at some length in part II.

Considering the accurate equation (2·2) once more, the method evolved by Gronwall, La Mer & Sandved (1928) for use in the theory of strong electrolytes was used by Levine

(1939) to obtain a solution for two spherical particles as an infinite series, and later Booth (1951) obtained a similar type of solution. However, both suffered from the disadvantage that the coefficients became extremely complicated, and an inordinate amount of computation would be required to obtain sufficient terms to make the solutions accurate over the wide ranges of the parameters which occur in practice. Furthermore, a great disadvantage of the Gronwall–La Mer–Sandved series is that it is difficult to calculate the radius of convergence, and in those cases where it can be found (or an upper bound found) it is so small as to restrict the application of the method. This latter difficulty was overcome by Levine for a single sphere, who used the series in an inverted form and showed that this has an infinite radius of convergence but the complexity of coefficients still remained.

3. Numerical solution

We now seek a numerical solution to (2·2) in the region outside two equal spheres of radius τ, where the distance between the centres is $s\tau$. Co-ordinate axes are fixed with the origin at the mid-point of the line of centres, and the x' axis along the line of centres.

The spherical boundaries may most simply be taken into account by considering the equation in dipolar co-ordinates (see MacRobert 1927) where

$$x' = \frac{c\sinh t}{\cosh t - \cos u}, \quad y' = \frac{c\sin u\cos v}{\cosh t - \cos u}, \quad z' = \frac{c\sin u\sin v}{\cosh t - \cos u}. \tag{3·1}$$

In these co-ordinates two equal spheres may be defined by $t = \pm t_0$, the radius of each being $c\,\mathrm{cosech}\,t_0$ and the distance between the centres $2c\coth t_0$. Thus if τ and s are known c and t_0 are uniquely determined by

$$4c^2 = \tau^2(s^2-4), \quad 2\cosh t_0 = s,$$

so that the dipolar transformation is fixed. The region outside the two spheres is given by (3·1) together with $-t_0 \leqslant t \leqslant t_0$, $0 \leqslant u \leqslant \pi$, $0 \leqslant v \leqslant 2\pi$. The solution of (2·2) is axially symmetric about the x' axis and so will be independent of v. Then (2·2) becomes

$$\frac{(\cosh t - \cos u)^3}{c^2\sin u}\left\{\frac{\partial}{\partial t}\left(\frac{\sin u}{\cosh t-\cos u}\frac{\partial\phi}{\partial t}\right) + \frac{\partial}{\partial u}\left(\frac{\sin u}{\cosh t-\cos u}\frac{\partial\phi}{\partial u}\right)\right\} = \sinh\phi, \tag{3·2}$$

together with

$$\phi = 0 \quad \text{at} \quad t = u = 0,$$
$$\phi = \Phi \quad \text{on} \quad t = \pm t_0.$$

ϕ is an even function of u and t, and the equation need only be considered in the region $0 \leqslant u \leqslant \pi$, $0 \leqslant t \leqslant t_0$ with the extra conditions

$$\frac{\partial\phi}{\partial u} = 0 \text{ on } u = 0,\ u = \pi; \quad \frac{\partial\phi}{\partial t} = 0 \text{ on } t = 0.$$

In order to obtain a numerical solution it is necessary to form the difference equation corresponding to (3·2) by expressing the derivatives in terms of finite differences. The region

$0 \leqslant u \leqslant \pi$, $0 \leqslant t \leqslant t_0$ is covered by a two-dimensional array of points lying on the intersection of lines $t = mB$ and $u = nA$ (figure 1). Then

$$\left(\frac{\partial\phi}{\partial u}\right)_0 = \frac{1}{A}[\mu\delta_u\phi_0 - \tfrac{1}{6}\mu\delta_u^3\phi_0 + \ldots],$$

$$\left(\frac{\partial\phi}{\partial t}\right)_0 = \frac{1}{B}[\mu\delta_t\phi_0 - \tfrac{1}{6}\mu\delta_t^3\phi_0 + \ldots],$$

$$\left(\frac{\partial^2\phi}{\partial u^2}\right)_0 = \frac{1}{A^2}[\delta_u^2\phi_0 - \tfrac{1}{12}\delta_u^4\phi_0 + \ldots],$$

$$\left(\frac{\partial^2\phi}{\partial t^2}\right)_0 = \frac{1}{B^2}[\delta_t^2\phi_0 - \tfrac{1}{12}\delta_t^4\phi_0 + \ldots],$$

where
$$\mu\delta_u\phi_0 = \tfrac{1}{2}(\delta_u\phi_{\frac{1}{2}} + \delta_u\phi_{-\frac{1}{2}}) = \tfrac{1}{2}(\phi_2 - \phi_4),$$
$$\delta_u^2\phi_0 = \delta_u\phi_{\frac{1}{2}} - \delta_u\phi_{-\frac{1}{2}} = \phi_2 + \phi_4 - 2\phi_0.$$

Similarly,
$$\mu\delta_t\phi_0 = \tfrac{1}{2}(\phi_1 - \phi_3), \quad \delta_t^2\phi_0 = \phi_1 + \phi_3 - 2\phi_0.$$

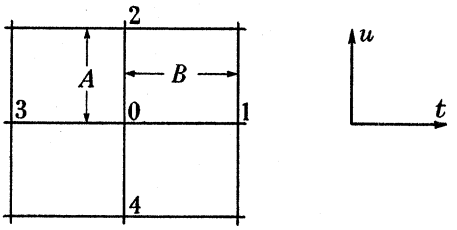

FIGURE 1

After substitution and division by the coefficient of ϕ_0 the equation in its final form becomes

$$\begin{aligned}
&\frac{A^2}{2(A^2+B^2)}\left[1 - \frac{B\sinh t}{2(\cosh t - \cos u)}\right]\phi_1 \\
&\quad + \frac{B^2}{2(A^2+B^2)}\left[1 + \frac{A\operatorname{cosec} u(\cos u\cosh t - 1)}{2(\cosh t - \cos u)}\right]\phi_2 \\
&\quad + \frac{A^2}{2(A^2+B^2)}\left[1 + \frac{B\sinh t}{2(\cosh t - \cos u)}\right]\phi_3 \\
&\quad + \frac{B^2}{2(A^2+B^2)}\left[1 - \frac{A\operatorname{cosec} u(\cos u\cosh t - 1)}{2(\cosh t - \cos u)}\right]\phi_4 \\
&\quad + \Delta_0 \\
&= \phi_0 + \frac{A^2B^2c^2}{2(A^2+B^2)(\cosh t - \cos u)^2}\sinh\phi_0, \qquad (3{\cdot}3)
\end{aligned}$$

where
$$\Delta_0 = \frac{1}{4(A^2+B^2)}\left[-\frac{1}{12}\left(\frac{1}{A^2}\delta_u^4\phi_0 + \frac{1}{B^2}\delta_t^4\phi_0\right) + \frac{1}{6B}\frac{\sinh t}{(\cosh t - \cos u)}\mu\delta_t^3\phi_0 - \frac{1}{6A}\frac{\operatorname{cosec} u(\cos u\cosh t - 1)}{\cosh t - \cos u}\mu\delta_u^3\phi_0 + \ldots\right]. \qquad (3{\cdot}4)$$

Henceforth (3·3) will for simplicity be written

$$a_1\phi_1 + a_2\phi_2 + a_3\phi_3 + a_4\phi_4 - \phi_0 - 2a_0c^2\sinh\phi_0 + \Delta_0 = 0, \qquad (3{\cdot}5)$$

where a_0, a_1, a_2, a_3 and a_4 are defined from (3·3).

This equation defines the relationship between all points on the mesh covering the region $0 \leqslant u \leqslant \pi$, $0 \leqslant t \leqslant t_0$, and the boundary conditions may also be rewritten as shown in figure 2.

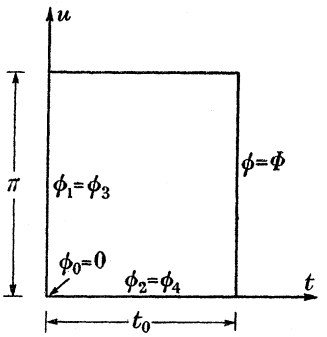

FIGURE 2

The solutions obtained here are solutions to (3·5) with $\Delta_0 \equiv 0$. The neglect of the higher differences will result in some solutions being only moderate approximations. However, it is possible to use these solutions to calculate Δ_0 and so obtain a better approximation as in the difference technique advocated by Fox (1947), and furthermore the errors in such solutions are probably less than in corresponding solutions obtained by the other methods available. Equation (3·5) is now in a form suitable for solution by relaxation, but the fact that the coefficients a_0, a_1, a_2, a_3 and a_4 are functions of u and t prohibits the solution by hand, and the calculations were carried out on the Manchester Electronic Computer.

The number of points covering the region, and hence the mesh lengths, were governed by the limited capacity of the high-speed storage of the machine. The final choice was a matrix of 144 (9×16) points including the boundary points, so that

$$A = \pi/15, \quad B = t_0/8.$$

An iterative method of successive approximations was adopted, and to begin the routine it was necessary to read an approximate solution to (3·5) into the machine. This set of function values had the correct values at points on the boundary and at the point representing infinity but was incorrect at all other points. In fact, the approximate solution was usually defined to have zero as its value at all points other than boundary points, or else a previous solution with the same value of Φ but different values of τ and s could be used. Since the solution was incorrect when the left-hand side of (3·5) (with $\Delta_0 = 0$) was calculated, the values were not everywhere zero. The aim of the iteration was to reduce those non-zero values or residuals to zero. This necessitated the solution of the equation

$$2a_0c^2 \sinh \phi_0^* + \phi_0^* = a_1\phi_1 + a_2\phi_2 + a_3\phi_3 + a_4\phi_4, \tag{3·6}$$

ϕ_0^* being the required new value. Since the process was iterative this equation need not be solved exactly at each iteration but only in the limit after an infinite number of iterations. A simpler equation may be constructed by assuming that

$$\phi_0^* = \phi_0 - \lambda_0,$$

where ϕ_0 was the existing value of the function at the pivotal point and λ_0 was small enough to neglect its square and higher powers. Then

$$\sinh \phi_0^* = \sinh (\phi_0 - \lambda_0) = \sinh \phi_0 - \lambda_0 \cosh \phi_0, \tag{3·7}$$

and on substitution into (3·6) and solving for λ_0 one obtained

$$\lambda_0 = \frac{\phi_0 - a_1\phi_1 - a_2\phi_2 - a_3\phi_3 - a_4\phi_4 + 2a_0c^2\sinh\phi_0}{1 + 2a_0c^2\cosh\phi_0}. \tag{3·8}$$

The Liebmann (1918) method of iteration was used, i.e. the quantity λ_0 was calculated and the function value adjusted before continuing to the next mesh point. For this method Frankel (1950) has shown that better convergence might be expected by over-relaxing—having found λ_0 to adjust the function value by $\alpha\lambda_0$, where $\alpha > 1$. This was found to be so in practice, and trial solutions were found using different values of α. The factor giving greatest convergence was $\alpha = 1{\cdot}5$, and this value was used for all subsequent solutions. Since (3·8) does not hold until λ_0 is small enough to justify the linearization in (3·7), the convergence might have been further improved by the use of an even greater value of α during the first iterations. However, this would have meant a change in α to $\alpha = 1{\cdot}5$ after a number of iterations, and the extra complication was thought to outweigh any advantage that might have been obtained.

To ensure complete control by the machine and eliminate any need for human intervention great care was taken to make the routine self-checking. Arithmetical checks were inserted wherever possible, and failure of such a check caused the machine to obey that sequence of instructions until the check was successful.

As a check on the convergence, $\Sigma\lambda_0^2$ was formed as the sweep over the whole mesh was in progress, and at the end of the interation tested against the sum obtained during the previous iteration. If it were less than the previous sum the new approximation was assumed to be better than its predecessor, and the new function values were stored instead of the previous set. If, however, the sum were greater, and this only happened if a fault had occurred, the iteration was repeated using the previous function values once more. The routine stopped and printed out the function values when $\Sigma\lambda_0^2$ was sufficiently small to ensure that the function values had settled down to their limiting values to at least three decimal places.

The routine evolved using all these checks was found to be foolproof, and the only cases of failure occurred when the machine fault was such that the sequence of instructions being obeyed were altered or obliterated. In all other cases once the approximate solution and parameter values had been supplied to the machine the whole calculation proceeded automatically until finally the required solution was printed out. Each complete iteration took 1 min 40 s to complete, and on an average it required twenty-five iterations to achieve the desired accuracy. Thus a solution could be obtained in about 40 min. This time could be reduced but only at the expense of further complication of the routine or the elimination of the checking procedure.

4. Parameter values

The mathematical problem of the solution of (2·2) is determined by the choice of four parameters, namely

(i) κ, which for a given electrolyte is a function of concentration and temperature,
(ii) ψ_0, the boundary value of the potential,
(iii) a, the radius of the colloidal particles, and
(iv) R, the separation of the two particles.

Actually in the physical problem the electrolyte concentration γ and ψ_0 are connected by the equation

$$\psi_0 = \text{constant} + \frac{kT}{ze} \ln \gamma. \tag{4·1}$$

Since γ is proportional to n, and n is proportional to κ^2 from (2·3), equation (4·1) may be rewritten

$$\Phi = \text{constant} + 2 \ln \kappa, \tag{4·2}$$

where

$$\Phi = ze\psi_0/kT.$$

The constant depends on the nature of the sol and thus if Φ and κ are chosen independently the same numerical solutions will be applicable to different sols.

The region of interest (Overbeek 1950) is for particles between 10^{-7} and 10^{-4} cm radius and values of κ between 10^5 and $10^{7·5}$ (corresponding to concentrations of a uni-univalent electrolyte in water from 10^{-5} N to 1 N), and thus the range of interest of $\tau = \kappa a$ is from 10^{-2} to $10^{3·5}$. The values considered here are in the middle of this range, i.e. between 1 and $10^{1·5}$. The values of the separation chosen are small or moderate, since for large separation the effect of interaction decreases and will become comparable with the error in the method, and although it would have been desirable to have obtained a solution with the two particles in contact with each other ($s=2$), the dipolar transformation unfortunately breaks down for this configuration. It has been shown that the Debye–Hückel solution is a good approximation for a single spherical particle for values of $\Phi \leqslant 1$, and thus one may hope that this still remains true in the case of two spheres. For large values of Φ the corrections to the P.B. equation may become appreciable and so the values of Φ chosen were in the middle of the range. The final values of the parameters chosen were

$$\left.\begin{aligned} \tau &= 1·0,\ 5·0,\ 15·0; \\ \tau(s-2) &= 0·5,\ 1·0,\ 1·5,\ 2·0,\ 3·0; \\ \Phi &= 2·0,\ 4·0,\ 6·0,\ 8·0. \end{aligned}\right\} \tag{4·3}$$

5. Results and discussion

A set of sixty solutions of the P.B. equation were obtained, each corresponding to one set of the parameter values given in (4·3). Considerations of space forbid the inclusion of the full solutions here, but a set of the sixty tables has been accepted by the Royal Society Depository. They may be consulted at the library of the Royal Society or photocopies can be obtained if so desired. The general behaviour of the distribution may be seen in figures 4, 5 and 6, where equipotentials have been constructed for three typical cases having the same values of the particle separation and surface potential but three different values of the particle radius. If the equipotential $\phi = 0·01$ is assumed to determine the outer limit of the double layer it is seen that the actual thickness of the layer increases only slightly as the radius increases. The effect of the interaction is to distort the equipotentials from the circular shape they would assume if only one spherical particle were present, and in figures 5 and 6 the parts of the equipotentials that have been omitted are circles with centres at the particle centre. Thus it may be seen from the figures that the effect of interaction is only appreciable in the region between the particles and becomes negligible around the 'outer' faces of the spheres. This is also demonstrated in figure 3, where the values of the potential function on

the line of centres diametrically opposed from the origin are compared with the corresponding solution for a single sphere and found to be in very good agreement. This solution is for $\Phi = 2{\cdot}0$, $\tau = 1{\cdot}0$ and the smallest value of the separation ($\tau(s-2) = 0{\cdot}50$), and if the

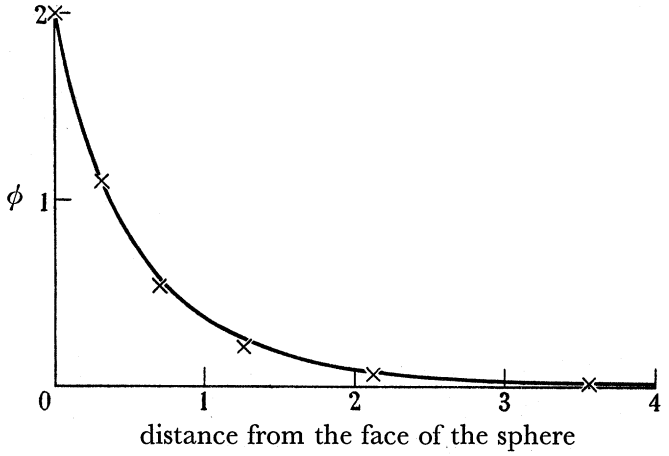

FIGURE 3

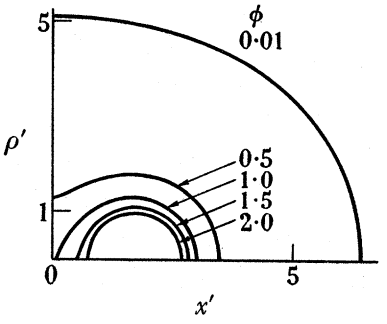

FIGURE 4

FIGURE 3. Comparison of the potential distribution for a single sphere with the distribution on the line of centres on the outer face of either of two spheres. ($\tau = 1$, $\tau(s-2) = 0{\cdot}5$, $\Phi = 2$.) ——, Single-sphere distribution; ×, two-sphere potential at mesh points on the line of centres.

FIGURE 4. Potential distribution for $\tau = 1$, $\tau(s-2) = 1{\cdot}5$, $\Phi = 2$.

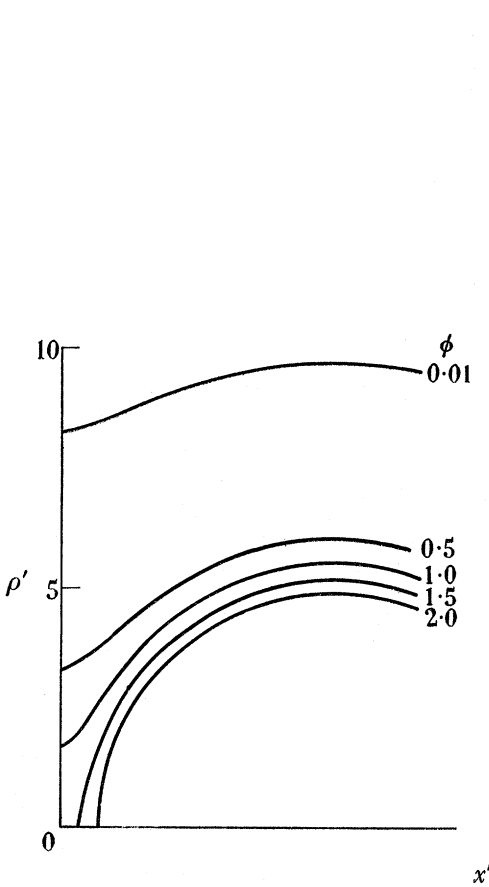

FIGURE 5. Potential distribution for $\tau = 5$, $\tau(s-2) = 1{\cdot}5$, $\Phi = 2$.

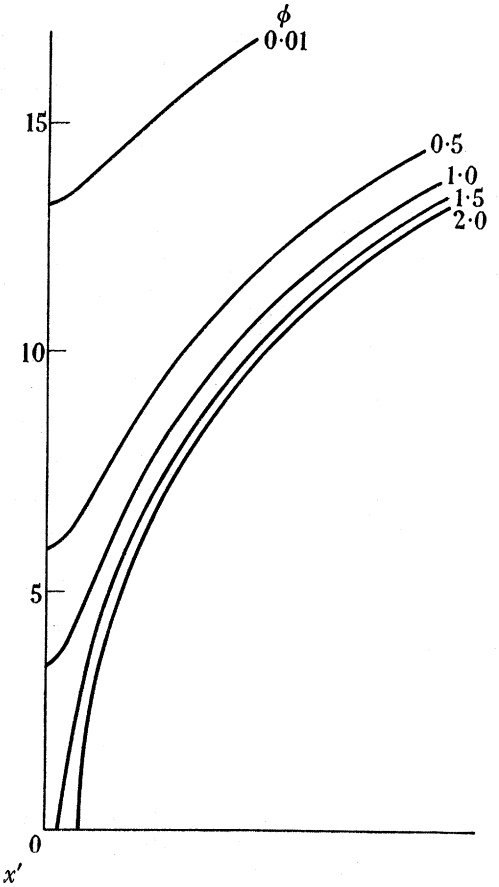

FIGURE 6. Potential distribution for $\tau = 15$, $\tau(s-2) = 1{\cdot}5$, $\Phi = 2$.

separation or radius is increased so that the other sphere is still further removed from this region its effect will be even less. For higher values of Φ the effect of interaction is still negligible on the outer face if $\tau = 5$ or $\tau = 15$, but becomes appreciable if $\tau = 1$. The fact that the interaction is only appreciable in the region between the particles counteracts in part the disadvantage of variable mesh length arising from the dipolar transformation. The mesh of points in the physical plane is formed by the intersection of two families of coaxial circles, and while the mesh length is small in the region between the particles the points becomes widely spaced on the other faces of the particles. However, we now see that the distribution about the outer faces is similar to that for a single sphere, and the complete potential may be found with greater accuracy by dividing the whole plane into an 'inner' and 'outer' region and using the solution for a single sphere in the outer region and the two-sphere solution in the inner region between the particles.

A general discussion of the potential distributions is impracticable because of the number of parameters involved, and we confine our remarks and tables to the distribution (a) along the line of centres and (b) in the median plane. In table 1 we have tabulated the potential

TABLE 1. POTENTIAL ON THE LINE OF CENTRES

τ	$\tau(s-2)$ \ $8t/t_0$	8	7	6	5	4	3	2	1	0
1	0·5	2·000	1·952	1·909	1·873	1·843	1·819	1·803	1·793	1·790
		4·000	3·823	3·673	3·548	3·448	3·371	3·316	3·284	3·274
		6·000	5·488	5·098	4·796	4·566	4·395	4·278	4·209	4·186
		8·000	6·826	6·088	5·575	5·206	4·944	4·768	4·666	4·633
	1·5	2·000	1·752	1·542	1·368	1·229	1·122	1·046	1·001	0·985
		4·000	3·367	2·877	2·495	2·201	1·982	1·830	1·741	1·711
		6·000	4·706	3·864	3·264	2·826	2·511	2·297	2·174	2·133
		8·000	5·691	4·496	3·719	3·177	2·798	2·544	2·398	2·350
	3·0	2·000	1·532	1·167	0·888	0·679	0·530	0·431	0·373	0·355
		4·000	2·926	2·172	1·626	1·231	0·954	0·771	0·667	0·633
		6·000	4·050	2·909	2·141	1·605	1·236	0·995	0·859	0·815
		8·000	4·863	3·384	2·457	1·830	1·404	1·127	0·971	0·920
5	0·5	2·000	1·970	1·945	1·923	1·906	1·893	1·884	1·878	1·877
		4·000	3·855	3·735	3·637	3·558	3·499	3·457	3·433	3·425
		6·000	5·518	5·158	4·885	4·678	4·527	4·423	4·363	4·343
		8·000	6·838	6·128	5·644	5·301	5·060	4·898	4·806	4·775
	1·5	2·000	1·833	1·693	1·579	1·488	1·418	1·368	1·338	1·327
		4·000	3·458	3·057	2·752	2·522	2·353	2·237	2·169	2·146
		6·000	4·748	3·991	3·475	3·109	2·850	2·677	2·577	2·544
		8·000	5·668	4·561	3·877	3·415	3·098	2·889	2·770	2·731
	3·0	2·000	1·615	1·318	1·089	0·915	0·787	0·700	0·649	0·632
		4·000	3·003	2·349	1·888	1·556	1·320	1·162	1·071	1·041
		6·000	4·042	3·021	2·368	1·921	1·612	1·408	1·292	1·255
		8·000	4·765	3·432	2·645	2·123	1·770	1·540	1·408	1·365
15	0·5	2·000	1·970	1·945	1·923	1·905	1·892	1·882	1·877	1·875
		4·000	3·857	3·737	3·640	3·562	3·502	3·461	3·436	3·429
		6·000	5·519	5·161	4·890	4·685	4·534	4·431	4·371	4·352
		8·000	6·838	6·131	5·649	5·308	5·068	4·907	4·815	4·786
	1·5	2·000	1·844	1·716	1·611	1·528	1·465	1·420	1·393	1·384
		4·000	3·471	3·083	2·791	2·572	2·412	2·303	2·238	2·217
		6·000	4·751	4·006	3·504	3·150	2·902	2·736	2·640	2·609
		8·000	5·661	4·568	3·899	3·451	3·145	2·943	2·829	2·791
	3·0	2·000	1·633	1·354	1·141	0·979	0·861	0·781	0·734	0·718
		4·000	3·016	2·385	1·946	1·633	1·412	1·264	1·179	1·152
		6·000	4·035	3·040	2·415	1·991	1·700	1·509	1·401	1·366
		8·000	4·740	3·437	2·680	2·185	1·852	1·635	1·513	1·473

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Table 2. Potential in the median plane

τ	$\tau(s-2)$	Φ \ $15u/\pi$	15	14	13	12	11	10	9	8	7	6	5	4	3	2	1
1	0·50	2	1·790	1·781	1·764	1·735	1·690	1·626	1·538	1·418	1·260	1·058	0·812	0·532	0·257	0·057	0·000
		4	3·274	3·252	3·214	3·149	3·054	2·923	2·746	2·516	2·222	1·857	1·421	0·933	0·452	0·102	0·001
		6	4·186	4·155	4·099	4·007	3·873	3·692	3·455	3·154	2·779	2·320	1·776	1·170	0·571	0·130	0·001
		8	4·633	4·598	4·533	4·426	4·273	4·068	3·802	3·468	3·055	2·553	1·959	1·296	0·637	0·146	0·001
	1·50	2	0·985	0·966	0·935	0·885	0·818	0·734	0·632	0·518	0·395	0·271	0·158	0·070	0·018	0·001	—
		4	1·711	1·679	1·626	1·542	1·427	1·281	1·108	0·910	0·696	0·480	0·282	0·125	0·032	0·002	—
		6	2·133	2·094	2·029	1·927	1·786	1·607	1·392	1·147	0·881	0·611	0·360	0·161	0·041	0·003	—
		8	2·350	2·309	2·239	2·128	1·975	1·781	1·546	1·277	0·984	0·685	0·406	0·182	0·047	0·003	—
	3·00	2	0·355	0·343	0·325	0·298	0·262	0·220	0·174	0·127	0·083	0·047	0·020	0·004	0·000	—	—
		4	0·633	0·614	0·582	0·534	0·471	0·396	0·314	0·230	0·151	0·085	0·037	0·011	0·001	—	—
		6	0·815	0·790	0·750	0·688	0·608	0·512	0·407	0·299	0·197	0·111	0·049	0·014	0·001	—	—
		8	0·920	0·893	0·848	0·780	0·689	0·582	0·463	0·341	0·225	0·127	0·056	0·016	0·002	—	—
5	0·50	2	1·877	1·873	1·865	1·850	1·826	1·789	1·733	1·649	1·520	1·327	1·047	0·676	0·274	0·028	—
		4	3·425	3·412	3·384	3·336	3·264	3·160	3·015	2·818	2·550	2·189	1·711	1·108	0·459	0·049	—
		6	4·343	4·321	4·273	4·192	4·072	3·910	3·696	3·420	3·065	2·613	2·038	1·329	0·562	0·062	—
		8	4·775	4·749	4·690	4·592	4·449	4·257	4·009	3·696	3·303	2·811	2·195	1·440	0·618	0·069	—
	1·50	2	1·327	1·309	1·276	1·223	1·146	1·042	0·910	0·749	0·564	0·367	0·186	0·060	0·007	—	—
		4	2·146	2·117	2·065	1·978	1·854	1·688	1·479	1·224	0·928	0·612	0·347	0·103	0·013	—	—
		6	2·544	2·510	2·448	2·347	2·200	2·007	1·762	1·465	1·119	0·745	0·390	0·130	0·017	—	—
		8	2·731	2·697	2·630	2·521	2·366	2·161	1·902	1·586	1·218	0·817	0·432	0·145	0·019	—	—
	3·00	2	0·632	0·614	0·582	0·533	0·467	0·386	0·297	0·205	0·122	0·057	0·018	0·003	—	—	—
		4	1·041	1·013	0·963	0·885	0·779	0·649	0·502	0·350	0·209	0·099	0·032	0·005	—	—	—
		6	1·255	1·223	1·165	1·073	0·947	0·793	0·617	0·433	0·262	0·125	0·041	0·006	—	—	—
		8	1·365	1·331	1·269	1·171	1·038	0·872	0·682	0·482	0·293	0·141	0·046	0·007	—	—	—
15	0·50	2	1·875	1·872	1·864	1·850	1·828	1·795	1·745	1·670	1·555	1·378	1·108	0·720	0·272	0·018	—
		4	3·429	3·417	3·392	3·347	3·279	3·182	3·045	2·858	2·602	2·254	1·781	1·159	0·453	0·032	—
		6	4·352	4·334	4·288	4·209	4·093	3·934	3·726	3·456	3·110	2·667	2·097	1·374	0·552	0·041	—
		8	4·786	4·764	4·707	4·609	4·468	4·279	4·035	3·727	3·340	2·856	2·245	1·481	0·607	0·047	—
	1·50	2	1·384	1·370	1·341	1·292	1·219	1·119	0·986	0·818	0·616	0·394	0·188	0·050	0·003	—	—
		4	2·217	2·193	2·144	2·061	1·940	1·778	1·569	1·308	0·996	0·648	0·316	0·087	0·006	—	—
		6	2·609	2·582	2·523	2·424	2·281	2·090	1·846	1·545	1·186	0·782	0·389	0·109	0·009	—	—
		8	2·791	2·763	2·700	2·593	2·441	2·238	1·981	1·663	1·284	0·855	0·431	0·123	0·010	—	—
	3·00	2	0·718	0·700	0·667	0·614	0·539	0·445	0·340	0·230	0·130	0·055	0·014	0·001	—	—	—
		4	1·152	1·126	1·074	0·991	0·876	0·731	0·563	0·386	0·220	0·094	0·024	0·002	—	—	—
		6	1·366	1·337	1·278	1·182	1·049	0·881	0·684	0·473	0·274	0·119	0·031	0·003	—	—	—
		8	1·473	1·443	1·381	1·280	1·140	0·961	0·751	0·523	0·306	0·134	0·036	0·004	—	—	—

distribution along the line of centres for most of the solutions and in table 2 the distribution in the median plane. The main use of table 2 is in obtaining the force between the particles, and this is demonstrated in part II. Both tables show clearly the effect of change of parameters on the potential distribution. It is also of interest to compare the solutions with results obtained from the two approximate methods that have been developed. One applies when the surface potential and particle radius are both small so that the series solution given by Levine & Dube (1940) (based on the Debye–Hückel approximation) is valid and the other when the particle radius is large and the separation small so that the region directly between the two spheres may be approximated to that between two parallel flat plates.

TABLE 3. INTERACTION OF TWO SPHERES IN THE CASE $\tau = 1$

Comparison with the solution by series at points in the median plane.

		value from series solution	ϕ/Φ obtained by numerical integration			
$\tau(s-2)$	u		$\Phi=2$	$\Phi=4$	$\Phi=6$	$\Phi=8$
0·50	π	0·952	0·895	0·819	0·698	0·579
	$2\pi/3$	0·858	0·813	0·731	0·615	0·509
	$\pi/3$	0·421	0·406	0·355	0·295	0·245
1·00	π	0·713	0·685	0·596	0·493	0·405
	$2\pi/3$	0·570	0·554	0·481	0·399	0·329
	$\pi/3$	0·174	0·171	0·150	0·126	0·106
1·50	π	0·508	0·493	0·428	0·356	0·294
	$2\pi/3$	0·383	0·367	0·321	0·268	0·223
	$\pi/3$	0·082	0·080	0·071	0·060	0·051
2·00	π	0·357	0·345	0·307	0·258	0·215
	$2\pi/3$	0·253	0·242	0·215	0·182	0·153
	$\pi/3$	0·040	0·039	0·035	0·030	0·026
3·00	π	0·176	0·178	0·159	0·136	0·115
	$2\pi/3$	0·112	0·110	0·099	0·085	0·073
	$\pi/3$	0·011	0·011	0·010	0·008	0·007

The value $\tau = 1$ is sufficiently small for the first method to apply for small values of Φ, and the solutions for this value of the radius are compared with results derived from tables given by Verwey & Overbeek (1948). These are based on the above-mentioned series of which they retained only the first three terms. The two sets of function values are compared at three points on the median plane $t = 0$ and the results given in table 3. It is seen that there is good agreement for the lowest value of Φ and the largest value of the separation, but that the differences grow (*a*) as Φ increases since the Debye–Hückel equation is then no longer a good approximation and (*b*) as the separation decreases when the higher terms in the series solution become appreciable. The potential distributions along the line of centres and in the median plane for the case $\tau = 1$ are shown in figures 7 and 8 for $\Phi = 2$ and different values of the separation. If we denote by ρ' the radial distance in the median plane, the origin being the intersection of the line of centres with the plane, then as ρ' increases the potential function drops rapidly to zero from its maximum (ϕ_d say) at the origin. This maximum ϕ_d is always less than the corresponding value for two flat plates and increases as the radius is increased, if Φ and the separation are both kept constant. This may be seen clearly in figure 9, where the potential distributions in the median plane are drawn for constant Φ and separation but for different values of the radius. We may also note that

even when $\tau = 15$ the potential function has dropped almost to zero at $\rho' = 12$, confirming that the region of appreciable interaction is confined to the region directly between the particles.

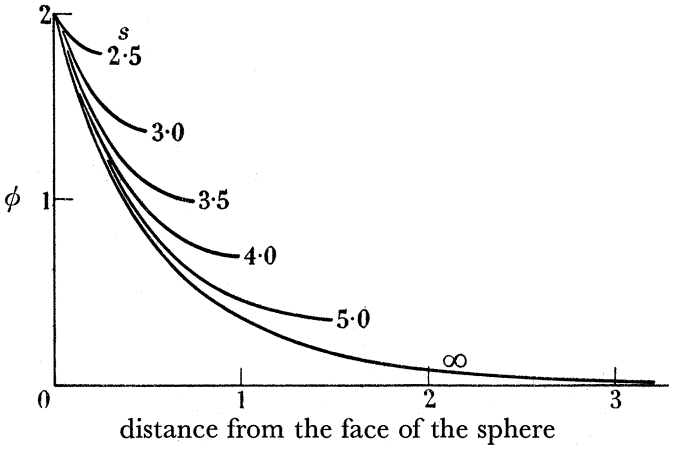

FIGURE 7. Potential function on the line of centres between two spherical particles for $\tau = 1$, $\Phi = 2$ and different values of the separation. Because of symmetry only one half is drawn.

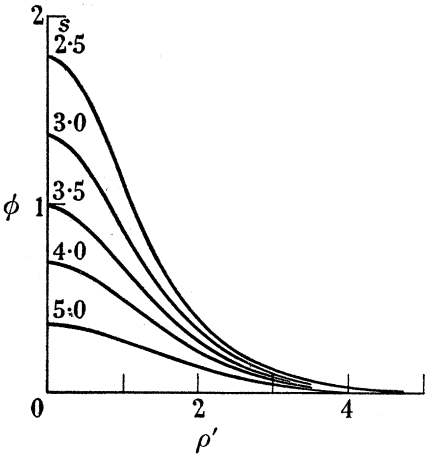

FIGURE 8. Potential function in the median plane of two spherical particles for $\tau = 1$, $\Phi = 2$ and different values of the separation.

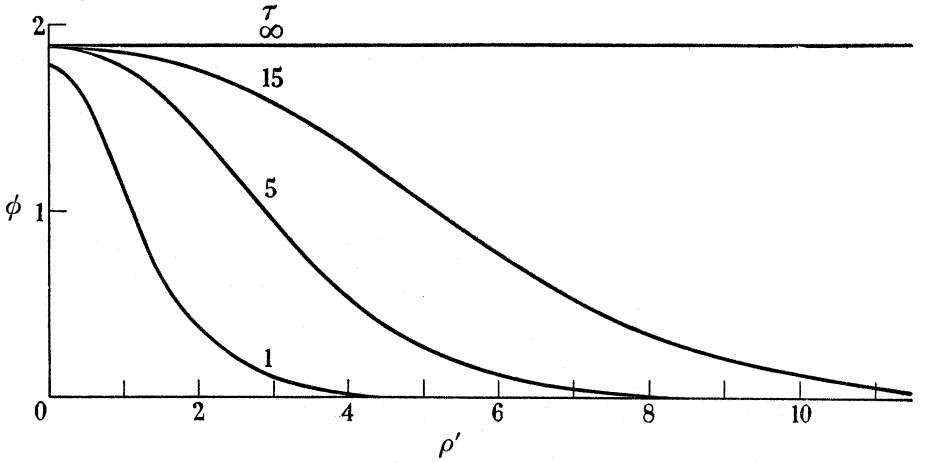

FIGURE 9. Potential function in the median plane of two spherical particles for $\Phi = 2$, $\tau(s-2) = 0{\cdot}5$ and different values of τ.

When $\tau = 15$ the region directly between the spheres may be expected to approximate to that between two flat plates, and in table 4 the values of ϕ_d for different values of Φ and the separation are compared with the corresponding values for two flat plates. There is good agreement when the separation is small, but the differences increase as the separation increases since the effect of the curvature of the spheres becomes important. In figure 10

TABLE 4. INTERACTION OF TWO SPHERES IN THE CASE $\tau = 15$

Comparison with the solution for two parallel plates at midpoint of line of centres.

		ϕ_d			
$\tau(s-2)$		$\Phi=2$	$\Phi=4$	$\Phi=6$	$\Phi=8$
0·50	2 spheres	1·875	3·429	4·352	4·786
	2 parallel plates	1·896	3·457	4·371	4·787
1·00	2 spheres	1·643	2·755	3·305	3·549
	2 parallel plates	1·663	2·773	3·309	3·535
1·50	2 spheres	1·384	2·217	2·609	2·791
	2 parallel plates	1·401	2·238	2·617	2·771
2·00	2 spheres	1·143	1·795	2·099	2·250
	2 parallel plates	1·156	1·815	2·106	2·223
3·00	2 spheres	0·718	1·152	1·366	1·473
	2 parallel plates	0·758	1·191	1·382	1·458

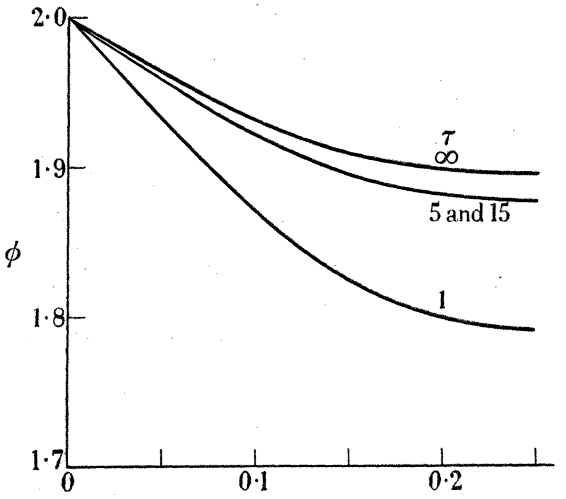

FIGURE 10. Potential function on the line of centres between two spherical particles for $\Phi = 2$, $\tau(s-2) = 0{\cdot}5$ and different values of τ. The curves for $\tau = 5$ and $\tau = 15$ are almost coincident. Because of symmetry only half is drawn.

the potential function along the line of centres is plotted for $\Phi = 2$, the smallest value of the separation ($\tau(s-2) = 0{\cdot}5$) and different values of the radius. The distributions for $\tau = 5$ and $\tau = 15$ are almost coincident and differ from that for two flat plates by less than 2 %. Even when $\tau = 1$ the error is never more than 7 %. However, for larger separation the agreement is not very good except for $\tau = 15$.

The charge distribution on the particle surface may be obtained from the potential, since if σ be the surface charge density

$$\sigma = -\frac{\epsilon}{4\pi}\left(\frac{\partial \psi}{\partial n}\right)_{\text{surface}}, \qquad (5{\cdot}1)$$

where $\partial/\partial n$ denotes differentiation along the outward normal to the particle surface. In dipolar co-ordinates this expression reads

$$\sigma = -\sqrt{\left(\frac{n\epsilon kT}{2\pi}\right)}\frac{\cosh t_0 - \cos u}{c}\left(\frac{\partial\phi}{\partial t}\right)_{t=t_0},$$
$$= -\sqrt{\left(\frac{n\epsilon kT}{2\pi}\right)}\frac{\partial\phi}{\partial n'}. \qquad (5{\cdot}2)$$

However, it is not possible to obtain an accurate tabulation of σ for all cases, or indeed over the whole of each particle, again because of the increase in mesh size around the 'outer' faces of the particles and also because of the inherent difficulties of numerical differentiation

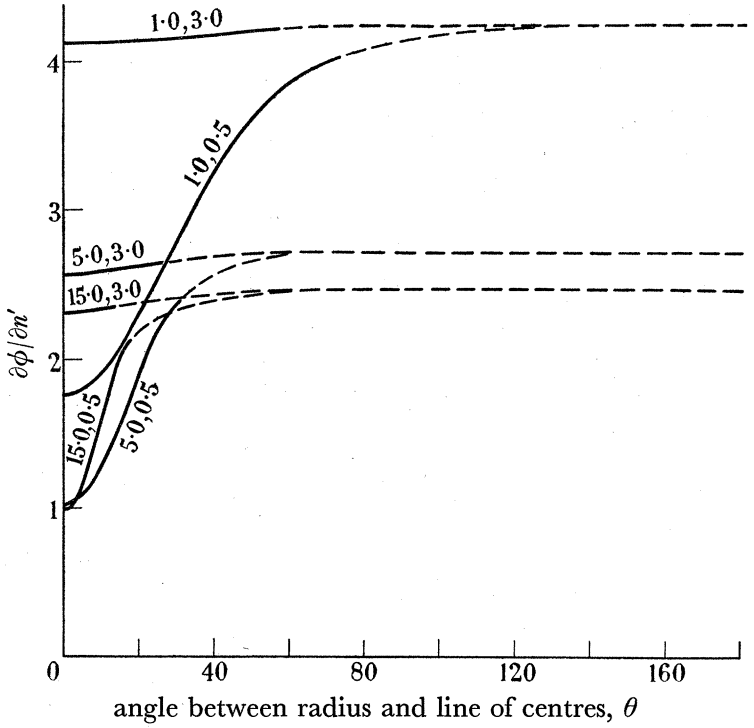

FIGURE 11. Variation of surface gradient of potential around a spherical particle:

$$(\sigma = -(n\epsilon kT/2\pi)^{\frac{1}{2}}\,\partial\phi/\partial n').$$

$\theta = 0$ at point of minimum separation. The numbers on the curves are the values of τ and $\tau(s-2)$ respectively.

at the end-point of a range of function values. We can determine σ fairly accurately on the 'inner' faces of the particles where both mesh lengths and gradients are small, but on the 'outer' part of the surfaces numerical differentiation gives progressively poorer results. However, at the point on the line of centres in the 'outer' region we may (as for the potential function) assume the effect of the outer particle to be negligible and σ then has the value corresponding to a single particle. Approximate values of σ in the intermediate region may be obtained by interpolating by means of a smooth curve. Some of the curves obtained in this way are shown in figure 11, where the variation of $\partial\phi/\partial n'$ around the particle is drawn for extreme values of the separation for each value of the radius and the same value ($\Phi = 2{\cdot}0$) of the surface potential.

References

Booth, F. 1951 *J. Chem. Phys.* **19**, 821.

Debye, P. & Hückel, E. 1923 *Phys. Z.* **24**, 185.

Debye, P. & Hückel, E. 1924 *Phys. Z.* **25**, 97.

Derjaguin, B. 1940 *Trans. Faraday Soc.* **36**, 203.

Fox, L. 1947 *Proc. Roy. Soc.* A, **190**, 31.

Frankel, S. 1950 *Math. Tab., Wash.*, **4**, 65.

Gronwall, T. H., La Mer, V. K. & Sandved, K. 1928 *Phys. Z.* **29**, 358.

Harmsen, G. J., Schooten, J. & Overbeek, J. Th. G. 1953 *J. Colloid Sci.* **8**, 72.

Hoskin, N. E. 1953 *Trans. Faraday Soc.* **49**, 1471.

Hoskin, N. E. & Levine, S. 1955 *Phil. Trans.* A, **248**, 449 (part II).

Langmuir, I. 1938 *J. Chem. Phys.* **6**, 893.

Levine, S. 1939 *J. Chem. Phys.* **7**, 831.

Levine, S. 1951 *J. Colloid Sci.* **6**, 1.

Levine, S. & Dube, G. P. 1940 *Phil. Mag.* **29**, 105.

Liebmann, H. 1918 *S.B. bayer. Akad. Wiss.* 385.

MacRobert, T. M. 1927 *Spherical harmonics.* London: Methuen.

Morris, R. J. 1952 Ph.D. Thesis (Manchester University).

Muller, H. 1928 *Kolloidbeihefte*, **26**, 257.

Overbeek, J. Th. G. 1950 *Advances in colloid sciences*, **3**. New York: Interscience.

Robinson, L. B. & Wood, L. A. 1946 *J. Chem. Phys.* **14**, 258.

Stigter, D. 1954 *Rec. Trav. chim. Pays-Bas*, **73**, 771.

Verwey, E. J. W. & Overbeek, J. Th. G. 1948 *Theory of the stability of lyophobic colloids.* Amsterdam: Elsevier Publishing Co.

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES