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THE INTERACTION OF TWO IDENTICAL SPHERICAL COLLOIDAL PARTICLES

II. THE FREE ENERGY

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By making use of the potential distribution in the electric double layers of two identical spherical colloidal particles, obtained numerically in the preceding paper (Hoskin 1955), the free energy of interaction of the two particles is calculated on the Manchester University Electronic Computer. Various equivalent formulae for both the interaction energy and the repulsive force are applied and compared. It is demonstrated that for the mesh used here, which is based on dipolar co-ordinates, the most accurate method is that which expresses the force in terms of the potential distribution on the median plane. The method of Derjaguin (1934, 1939) for determining the free energy, which treats two spherical particles as consisting of sections of two infinite parallel plates, is shown to yield a good approximation over a wide range of the relevant parameters. Three convenient methods of evaluating the free energy, which are based on the Derjaguin formula, are developed. These are suitable at (i) large particle separations, (ii) small surface potentials and (iii) large surface potentials.

1. INTRODUCTION

Two approximate methods of determining the free energy of interaction of the double layers of two spherical colloidal particles have been developed. The first is based on a series solution of the linear Debye–Hückel equation, which was obtained by Levine (1939) and applied by Derjaguin (1940) and Verwey & Overbeek (1948). This approach is applicable when the potential at the surface of the particles is of the order of 50 mV or less and the thickness of the double layers, $1/\kappa$, is not less than about one-fifth of the particle radius a . The second method was originally proposed by Derjaguin (1934, 1939), who first applied it to small surface potentials. Later it was extended independently by Derjaguin & Landau (1941) and Verwey & Overbeek (1948) to larger potentials. Derjaguin replaced the two spheres by a set of parallel rings, each pair of rings being treated as sections of infinite parallel plates. This method can be used if the thickness of the double layer is small compared with the particle radius ($a > 5/\kappa$, say) and the particles are not too far apart, i.e. the diffuse

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layers do overlap to a slight degree. Fortunately, at such large separations the interaction energy is also very small, and so the latter limitation is generally of little importance for stability properties. In this paper we shall obtain numerically the free energy of interaction by making use of the potential distributions in the interpenetrating double layers of the two spherical particles for the sixty different cases computed in the preceding part I (Hoskin 1955). These numerical calculations will be used to investigate the accuracy and range of validity of the two approximate theoretical methods described above.

Theoretically, the free energy may be obtained by two separate, though fundamentally equivalent, procedures: (i) directly from the potential distribution by the appropriate integration either over the volume external to the two spheres or over the surface of the particles; (ii) indirectly by first obtaining the force of repulsion from the potential distribution and then integrating the force with respect to the distance between the particles. The relation connecting the free energy and potential distribution may be expressed in various forms, and the equivalence of these has been proved by Casimir (1948) and later by Levine (1950, 1951) and Ikeda (1953). However, all the expressions involve numerical differentiation at the particle surface which may give rise to large errors for large values of the surface potential, since gradients of the potential function then vary rapidly and become large in the immediate neighbourhood of the particle. Also, the mesh size and hence the errors increase with the particle radius or the separation. Furthermore, we need to subtract the energy at infinite separation of the particles, and this usually means forming the difference between two large quantities, already subject to some error, to obtain a much smaller one. Nevertheless, in order to assess the usefulness of the various relations, it was felt worth while to evaluate the free energy for the lowest parameter values by all the methods available. It should be emphasized that some of the disadvantages quoted in this paper are mainly due to the manner in which the potential distribution has been found and do not preclude the use of the various equivalent formulae with different distributions of mesh points.

The force of repulsion between the particles can be obtained either by generalizing the considerations of Frumkin & Gorodetskaya (1938), Langmuir (1938) and Derjaguin & Landau (1941) for two parallel plates or by differentiating directly the formula for the free energy with respect to the particle separation. One form for the force can be expressed in terms of the potential distribution on the median plane, and *one of the main conclusions in the present paper is that this yields the most accurate value for the free energy of interaction.* (This is designated in the text as method III.) Indeed, among the various numerical methods investigated, this is the only reliable one for a considerable range of the relevant parameters, with the particular mesh used in part I. It seems likely that this formula for the force across the median plane will lend itself most readily to numerical methods in general. Two reasons for the superiority over the expressions for the free energy referred to above may be cited. First, the error in the potential is smallest in the region of the median plane, and secondly, no subtractions are necessary. Indeed, the effect of errors is decreased rather than increased when integration with respect to the separation is carried out to obtain the free energy. A second form for the force is described in terms of the potential gradient at the particle surface, but this suffers from the same defects as the corresponding expression for the free energy.

A second striking result is *the verification of the accuracy of the Derjaguin method* over a large range of the parameters on which the free energy depends, the error being of the order of 10 % or less if $\kappa a \geq 5$. An analysis of the nature of the approximations in this method suggests that its success is partly due to the fortunate cancellation of errors. It would probably be very much worth while, although by no means an easy task, to extend the investigations further, with a view to finding an analytical expression for the correction to the approximate formula for the free energy, which is based on the Derjaguin theory. In order to test the accuracy of this theory, we endeavoured to utilize the calculations of Verwey & Overbeek given in their table XVI (1948, p. 141), but found that interpolation of their figures was unreliable. To construct their table, these authors extended the original Derjaguin formula to larger potentials and then carried out a tedious graphical integration. In view of the validity of the Derjaguin approach for $\kappa a \geq 5$, we considered that it was very desirable to devise more convenient methods of computing the Derjaguin formula for the free energy. Three different types of series for the free energy of interaction of two spherical particles, based on the Derjaguin theory, have been developed. These employ convenient expansions for the free energy of two plates which have been obtained by Levine & Suddaby (1951 *a, b*, 1952). One method is suitable at large separations, the second at small surface potentials and the third at large surface potentials. Suitable numerical tables of the coefficients in these expansions are given. The use of these series enables almost the whole range of the relevant parameters (subject to the condition $\kappa a \geq 5$, say) to be covered in an adequate manner except, perhaps, when the separation is small and the surface potential lies between 50 and 100 mV.

We may comment as follows on the value of the numerical work carried out on the electronic computer, the results of which are presented in this paper. At present, the main purpose of the above calculations would be to develop stability relations of colloidal systems. Since this could form the subject-matter of several papers we shall only suggest to what extent such an objective can be attained by applying the results in the present paper. In most hydrophobic sols, the radius of the particles is usually larger than $10 m\mu$ and the concentration of electrolyte in the region of instability appreciably greater than $\frac{1}{100} N$ if the (inorganic) coagulating ion is univalent. This means that the region where the system becomes unstable usually corresponds to $\kappa a > 5$, and it is in this range that the Derjaguin theory yields reasonable results. Provided the surface potential is very nearly uniform, the present calculations should be adequate for most sols when the dispersion medium is a 1-1 electrolyte. In this connexion we should bear in mind that in order to determine the stability properties, the van der Waals–London attraction must be added to the repulsion between the double layers, and the error in the theoretical value of the constant in this attraction is considerably greater than 10 %. The obvious gap in the theoretical knowledge about the electrical interaction energy is at small values of κa (< 5) and surface potentials greater than $(50/z)$ mV where z is the valency of the coagulating ion. This is particularly pertinent if the valency of the coagulating ion is greater than one and the particle radius is not large. By judicious interpolation, it should be possible to obtain considerable information concerning stability conditions for small κa . However, since further computations are desirable at small values of κa , such a program of work has been undertaken with a view to applying the results to stability conditions.

All undefined symbols will have the same meaning as in part I, and again a dash will be used whenever distances are measured in units of $1/\kappa$, the characteristic thickness of the double layer.

2. EXPRESSIONS FOR THE FREE ENERGY

Two equivalent forms for the free energy were used. The first was originally obtained by Verwey & Overbeek (1948) in the special case of two parallel plates, and its general form was given by Levine (1951). Let W be the ordinary electrostatic energy associated with the double layers and $\Delta\Pi$ the difference between the 'ideal' osmotic pressure of the ions at a point in the diffuse layers and the corresponding pressure at infinity. Then the free energy of the double layers is

$$F = -W - \int_V \Delta\Pi dv. \quad (2.1)$$

In the case of a symmetrical binary electrolyte this may be written as

$$F = -\frac{\epsilon}{8\pi} \int_V |\nabla\psi|^2 dv - 2nkT \int_V \left(\cosh \frac{ze\psi}{kT} - 1 \right) dv \quad (2.2)$$

$$= -\frac{nkT}{\kappa^3} \int_{V'} [|\nabla'\phi|^2 + 2(\cosh\phi - 1)] dv'. \quad (2.3)$$

It is convenient to introduce the non-dimensional quantity $F^* = \kappa^3 F / nkT$ and to transform to dipolar co-ordinates, since the potential distributions are known on a mesh formed by the two sets of coaxial circles, which are co-ordinate curves in this system. Equation (2.3) then reads

$$F^* = -4\pi c^3 \int_0^{t_0} dt \int_0^\pi \left[\frac{(\cosh t - \cos u)^2}{c^2} \left\{ \left(\frac{\partial\phi}{\partial t} \right)^2 + \left(\frac{\partial\phi}{\partial u} \right)^2 \right\} + 2(\cosh\phi - 1) \right] \frac{\sin u du}{(\cosh t - \cos u)^3}. \quad (2.4)$$

The corresponding expression, F_0^* say, for a single spherical particle has already been computed numerically by Hoskin (1953). We shall refer to the use of (2.4) as method I.

The second expression for the free energy is the Lippmann equation, introduced by Derjaguin (1940) and Verwey & Overbeek (1948). Its general equivalence to the form (2.1) was proven by Levine (1951). It reads

$$F = -2 \int_{S_p} dS \int_0^{\psi_0} \sigma d\psi = -\frac{4nkT}{\kappa^3} \int_{S_p'} dS' \int_0^\phi \frac{\partial\phi}{\partial n} d\phi, \quad (2.5)$$

where S_p is the surface of one of the particles. Transforming to dipolar co-ordinates we may rewrite (2.5) as

$$F^* = -8\pi c \int_0^\pi \frac{\sin u du}{(\cosh t_0 - \cos u)} \int_0^\phi \left(\frac{\partial\phi}{\partial t} \right)_{t=t_0} d\phi, \quad (2.6)$$

the use of which will be designated as method II.

The physical quantity of interest, the free energy of interaction, is the change in the free energy as the particles are brought from infinite separation to their given configuration. Thus, we introduce the non-dimensional quantity

$$\Delta F^* = F^* - 2F_0^*. \quad (2.7)$$

This function was evaluated, but the results were in general rather unsatisfactory. The main cause for this failure was that F^* and $2F_0^*$ are almost equal, so that ΔF^* is much less than F^* .

For example, for the cases with $\tau = 1$, $\Phi = 2$ the largest value of ΔF^* (that for smallest separation) was roughly 10% of F^* , and the corresponding value of ΔF^* for the largest value of the separation was only about 2% of F^* . This ratio becomes even smaller as Φ is increased, and it may be seen that any errors occurring in the separate evaluation of F^* and F_0^* have their effect increased enormously as a result of the subtraction. An additional objection to method II is that it involves the surface charge which cannot be determined with any reliance over the whole of the particle surface (see part I). The disadvantage of dipolar co-ordinates in calculating the free energy by means of (2.4) or (2.6) is essentially due to the manner in which the mesh size varies throughout the volume V . In the region between the two particles the mesh length is smallest, whereas in the regions on the outer sides of the particles the mesh length is much too large to give any reasonable accuracy.

3. FORCE BETWEEN THE PARTICLES

To determine this force, we may start with the general considerations of Coolidge & Juda (1946) (compare also Stratton 1941, pp. 97–103). Making use of the Poisson–Boltzmann equation, we may write

$$\nabla \cdot \mathbf{T} = \rho \mathbf{E} = \frac{\epsilon}{4\pi} \nabla^2 \psi \nabla \psi = 2nze \sinh \phi \nabla \psi = \nabla \Pi, \quad (3.1)$$

where $\mathbf{T} = (\epsilon/8\pi) (2\mathbf{E}\mathbf{E} - E^2\mathbf{I})$ is the familiar stress tensor in electrostatics, \mathbf{I} being the unit tensor, $\mathbf{E} = -\nabla\psi$ is the electric field, ρ is the (volume) charge density, and E is the magnitude of the vector \mathbf{E} . Consider any simply (or multiply) connected volume v in the double layers bounded by a surface (or surfaces) S . Then we have (Stratton 1941, p. 103)

$$0 = \int_v (\nabla \cdot \mathbf{T} - \nabla \Pi) dv = \int_S \left[\frac{\epsilon}{4\pi} \{ (\mathbf{E} \cdot \mathbf{n}) \mathbf{E} - \frac{1}{2} E^2 \mathbf{n} \} - (\Pi - \Pi_0) \mathbf{n} \right] dS, \quad (3.2)$$

where \mathbf{n} is the unit outward normal vector to the surface S . It is convenient to add on $\Pi_0 \int_S \mathbf{n} dS = 0$ to the right-hand member of (3.2).

Let us now consider the volume contained by a large hemisphere, with median plane as base, but excluding the particle, centre O , contained inside. Then we may apply (3.2) to this volume and S consists of a section of the median plane S_m , the surface of the particle S_p and the hemisphere S_h . If we now increase the radius of the hemisphere so that all parts of its surface move off to infinity, then the integral over S_h will tend to zero, since the potential diminishes exponentially at large distances from O . On S_p , ϕ and therefore Π are constant, $\int_{S_p} \mathbf{n} dS = 0$, and if we assume $\psi_0 > 0$, $\mathbf{E} = -E\mathbf{n}$. On S_m , $\mathbf{E} \cdot \mathbf{n} = 0$ and \mathbf{n} is parallel to the line or centres, OO' say, of the two particles. Hence (or by axial symmetry) the vector which is obtained when integrating over the surface S_p also points along the line of centres. We therefore derive that

$$-\int_{S_m} \left(\frac{\epsilon}{8\pi} E^2 + \Pi - \Pi_0 \right) dS = -\frac{\epsilon}{8\pi} \left| \int_{S_p} E^2 \mathbf{n} dS \right| = \frac{\epsilon}{8\pi} \int_{S_p} E^2 \cos \theta dS, \quad (3.3)$$

where we now integrate over the whole median plane in the left-hand member, and if P is a point on the particle surface, θ is the angle between OP and OO' .

In the case of two parallel plates (i.e. when the particles become infinitely large), $E = 0$ at the median plane, and the left-hand member of (3.3) reduces to the expression obtained by Frumkin & Gorodetskaya (1938) and Langmuir (1938) for the force between the plates. This suggests that we identify (3.3) with the force of repulsion between the two particles. The left-hand member of (3.3) can be interpreted as the total force acting across the median plane, consisting of the osmotic pressure and the electrostatic stress. The right-hand member of (3.3) consists only of the electrostatic stress acting across the particle surface. The osmotic term vanishes, since the osmotic force at any point on the particle surface is balanced by that acting at the other end of the diameter. In order to prove that the two equivalent expressions in (3.3) actually represent the force between the particles, we must obtain these results by differentiating the expression (2.1) for F with respect to the separation R . This is carried out in the appendix where we consider the case of two colloidal particles P and P' say, which are of arbitrary shape and have a uniform (positive) surface potential ψ_0 which is independent of mutual separation and orientation.

Making use of the left-hand member of (3.3), the force between two spherical particles may be written as

$$-\frac{dF}{dR} = 2nkT \int_{s_m} \left(\cosh \frac{ze\psi}{kT} - 1 \right) dS + \frac{\epsilon}{8\pi} \int_{s_m} |\nabla\psi|^2 dS. \quad (3.4)$$

We introduce a non-dimensional quantity

$$f^* = -\frac{\kappa^2}{nkT} \frac{dF}{dR} = -\frac{dF^*}{dR^*}$$

and transform to dipolar co-ordinates. Equation (3.4) then reads

$$f^* = 2\pi \int_0^\pi \left\{ \left(\frac{\partial\phi}{\partial u} \right)^2 + \frac{2c^2(\cosh\phi - 1)}{(1 - \cos u)^2} \right\} \sin u \, du, \quad (3.5)$$

noting that $t = 0$ and $\partial\phi/\partial t = 0$ at the median plane. The application of (3.5) is referred to as method III. Alternatively, if we make use of the right-hand member of (3.3) and transform to dipolar co-ordinates, we obtain

$$f^* = \int_0^\pi \frac{(\cosh t_0 \cos u - 1)}{(\cosh t_0 - \cos u)} \left(\frac{\partial\phi}{\partial t} \right)_{t=t_0}^2 \sin u \, du, \quad (3.6)$$

the application of which will be called method IV.

4. DERJAGUIN'S METHOD

The basic formula in this method can be expressed in the form

$$\Delta F^* = \frac{\pi a \kappa^2}{nkT} \int_{R^*}^\infty \Delta F_p(R^*) \, dR^*, \quad (4.1)$$

where $\Delta F_p(R^*)$ is the free energy of interaction per unit area of two parallel plates at a separation $R - 2a$ and $R^* = \kappa(R - 2a) = \tau(s - 2)$. For large R we may apply a convenient expansion for the free energy of two parallel plates, which has been obtained by Levine & Suddaby (1951*a, b*). The first three terms in this expansion read

$$\Delta F_p(R^*) = \frac{64nkT}{\kappa} \Gamma \left[1 - \Gamma(2R^* - 3 + 4\delta) + 8\Gamma^2 \left\{ R^{*2} + R^* \left(4\delta - \frac{5}{2} \right) + 1 - 5\delta + 4\delta^2 - 2\mu \right\} + \dots \right], \quad (4.2)$$

where $\Gamma = \tanh^2(\frac{1}{4}\Phi) e^{-R^*}$, $\delta = \cosh \frac{1}{2}\Phi / \sinh^2 \frac{1}{2}\Phi$ and $\mu = \delta / \sinh^2 \frac{1}{2}\Phi$.

Integration of (4.2) yields

$$\Delta F^* = 64\pi\tau\Gamma[1 - \Gamma(R^* - 1 + 2\delta) + \frac{8}{3}\Gamma^2\{R^{*2} + R^*(4\delta - \frac{11}{6}) + \frac{7}{18} - \frac{11}{3}\delta + 4\delta^2 - 2\mu\} + \dots]. \quad (4.3)$$

Application of this result will be known as method *Va*.

For small Φ ($\psi_0 < 50$ mV) we may apply a second series for $\Delta F_p(R^*)$ which is expressed in powers of Φ and which reads

$$\Delta F_p(R^*) = \frac{2nkT}{\kappa}\Phi^2[1 - \tanh \frac{1}{2}R^* + \frac{1}{48}\{1 - 24G(\frac{1}{2}R^*)\}\Phi^2 + \frac{1}{5760}\{1 - 1920H(\frac{1}{2}R^*)\}\Phi^4 + \dots], \quad (4.4)$$

TABLE 1

x	$-10^3 B(x)$	$10^5 C(x)$	x	$-10^3 B(x)$	$10^5 C(x)$
0	10.42	30.38	1.1	5.019	23.13
0.05	11.35	29.96	1.2	4.157	19.16
0.10	12.09	30.00	1.3	3.423	15.64
0.15	12.62	30.72	1.4	2.805	12.65
0.20	12.96	31.91	1.5	2.291	10.15
0.25	13.13	33.40	1.6	1.867	8.118
0.30	13.13	35.04	1.7	1.519	6.477
0.35	12.99	36.67	1.8	1.235	5.164
0.40	12.73	38.12	1.9	1.004	4.118
0.45	12.36	39.27	2.0	0.8158	3.288
0.50	11.90	40.05	2.1	0.6632	2.630
0.55	11.38	40.38	2.2	0.5394	2.107
0.60	10.81	40.25	2.3	0.4388	1.692
0.65	10.21	39.67	2.4	0.3572	1.361
0.70	9.584	38.68	2.5	0.2909	1.097
0.75	8.959	37.33	2.6	0.2371	0.8771
0.80	8.329	35.67	2.7	0.1933	0.7169
0.85	7.716	33.79	2.8	0.1577	0.5809
0.90	7.122	31.75	2.9	0.1287	0.4713
0.95	6.552	29.61	3.0	0.1051	0.3828
1.0	6.010	27.43	∞	0	0

where $G(\frac{1}{2}R^*)$ and $H(\frac{1}{2}R^*)$ are certain functions which are readily integrated with respect to R^* (Levine & Suddaby 1951*a*, equation (35)). We obtain therefore

$$\Delta F^* = 8\pi\Phi^2\tau[\ln(1 + e^{-R^*}) + B(\frac{1}{2}R^*)\Phi^2 + C(\frac{1}{2}R^*)\Phi^4 + \dots], \quad (4.5)$$

where

$$B(x) = \frac{1}{96}[-1 + \tanh^2 x - x\{2 - \tanh x(2 + \operatorname{sech}^2 x)\}]$$

$$\text{and } C(x) = \frac{1}{5760}\left[\frac{7}{4} - x + \frac{15}{8}\{2x^2 \operatorname{sech}^6 x + x \tanh x(3 - \frac{14}{3} \tanh^2 x + \frac{11}{5} \tanh^4 x) - \frac{1}{15} \tanh^2 x(11 + 3 \tanh^2 x)\}\right].$$

Values of $B(x)$ and $C(x)$ are given in table 1. The first term on the right-hand side of (4.5) was originally obtained by Derjaguin (1940) when he applied the linear Debye-Hückel equation to the case of small potentials. We shall refer to the use of (4.5) as method *Vb*.

Finally, we shall develop a third method of evaluating the integral in (4.1), which is particularly suitable for large surface potentials, provided R^* is not too small. Consider two parallel (infinite) colloidal plates, at potential ψ_0 and separation $2d$, and let $\phi_m = ze\psi_m/kT$, where ψ_m is the potential at the median plane. It is convenient to introduce the substitution

$$k = \frac{1}{\cosh(\frac{1}{2}\phi_m)}, \quad u_0 = \sin \phi_0 = \frac{\cosh(\frac{1}{2}\phi_m)}{\cosh(\frac{1}{2}\Phi)}, \quad (4.6)$$

which was used by Derjaguin & Landau (1941). Then in the case of a binary, symmetrical electrolyte, the solution of the Poisson–Boltzmann equation leads to the relation

$$\Theta = \kappa d = k[K(k) - F(k, \phi_0)], \quad (4.7)$$

where

$$F(k, \phi_0) = \int_0^{u_0} \frac{du}{\sqrt{\{(1-u^2)(1-k^2u^2)\}}} \quad (4.8)$$

is the elliptic integral of the first kind and $K(k) = F(k, \frac{1}{2}\pi)$. It is readily verified that

$$\Theta = kK(k) - \frac{1}{H} - \frac{1}{6} \left(1 + \frac{1}{k^2}\right) \frac{1}{H^3} - \frac{1}{5} \left(\frac{3}{8k^4} + \frac{3}{8} + \frac{1}{4k^2}\right) \frac{1}{H^5} + \dots, \quad (4.9)$$

where $H = \cosh \frac{1}{2}\Phi$. Making use of the expression for the force per unit area between the two plates, as first given by Frumkin & Gorodetskaya (1938) and Langmuir (1938), the free energy of interaction per unit area of the plates is

$$\Delta F_p(2\kappa d) = 4nkT \int_{2d}^{\infty} \left(\frac{1}{k^2} - 1\right) dR = \frac{8nkT}{\kappa} \int_k^1 \left(\frac{1}{k^2} - 1\right) \frac{d\Theta}{dk} dk \quad (4.10)$$

$$= \frac{8nkT}{\kappa} \left[\frac{2E(k)}{k} - 2 - \left(\frac{1}{k} - k\right) K(k) + \frac{1}{12} \left(1 - \frac{1}{k^2}\right)^2 \frac{1}{H^3} + \frac{1}{20} \left(1 - \frac{1}{k^2}\right)^2 \left(1 + \frac{1}{k^2}\right) \frac{1}{H^5} + \dots \right], \quad (4.11)$$

where $E(k)$ is the complete elliptic integral of the second kind. The first term in this expansion in powers of $1/H$ has been obtained by Derjaguin & Landau (1941). A completely equivalent series† has been derived by Levine & Suddaby (1952), who chose the modulus $l = \exp(-\phi_m)$ and expanded in powers of $\exp(-\frac{1}{2}\Phi)$ rather than $(1/H)$.

When substituting (4.11) into (4.1) we identify $2kd$ with R^* and so obtain

$$\begin{aligned} \Delta F^* &= \frac{2\pi a \kappa^2}{nkT} \int_k^1 \Delta F_p(R^*) \frac{d\Theta}{dk} dk \\ &= 16\pi\tau \left[f_1(k) + \frac{f_2(k)}{H^3} + \frac{f_3(k)}{H^5} + \dots \right], \end{aligned} \quad (4.12)$$

where $f_1(k) = \frac{1}{2}(1-k^2) K^2(k) - 2\{E(k) - k\} K(k) + \int_k^1 \frac{1}{k} K^2(k) dk$,

$$f_2(k) = \frac{1}{108} \left[20 + \frac{1}{k^3} \{16(2-k^2) E(k) - (17-9k^2)(1-k^2) K(k) - 36k\} \right]$$

and $f_3(k) = \frac{1}{20} \left[\frac{517}{225} - \frac{(1-k^2)}{k^4} \left(\frac{37}{25} + \frac{196}{225} k^2 - k^4 \right) K(k) \right.$

$$\left. + \frac{8}{225k^4} (81 + 44k^2 - 48k^4) E(k) - \frac{3}{k^4} - \frac{2}{k^2} \right].$$

Values of $kK(k)$, $f_1(k)$, $f_2(k)$ and $f_3(k)$ for various k are given in table 2. The integral in the formula for $f_1(k)$ is evaluated numerically. The use of (4.12) is designated as method Vc. When we do not distinguish between the three methods described above for evaluating (4.1) we shall refer to method V.

† This alternative series should read (in the present notation)

$$\Delta F_p(2\kappa d) = \frac{4nkT}{\kappa} \left[l^3 \left(2 + l - \frac{3}{l} \right) K(l) + 4l^{-3} E(l) - 4 + \frac{1}{12} \frac{(1-l)^4}{l^2} e^{-\frac{3}{2}\Phi} + \frac{1}{20} \frac{(1-l)^3 (1-l^3)}{l^3} e^{-\frac{5}{2}\Phi} + \dots \right].$$

TABLE 2

k	$kK(k)$	$f_1(k)$	$f_2(k)$	$f_3(k)$
0	0	∞	∞	∞
0.05	0.07859	5.162	1612	3.285×10^5
0.10	0.1575	3.600	184.7	9571
0.15	0.2370	2.743	49.79	1172
0.20	0.3174	2.171	18.95	257.9
0.25	0.3991	1.755	8.675	78.01
0.30	0.4824	1.435	4.442	28.76
0.35	0.5679	1.182	2.447	12.11
0.40	0.6560	0.9753	1.415	5.600
0.45	0.7474	0.8046	0.8447	2.766
0.50	0.8429	0.6616	0.5141	1.432
0.55	0.9434	0.5406	0.3156	0.7640
0.60	1.050	0.4375	0.1934	0.4146
0.65	1.166	0.3492	0.1171	0.2256
0.70	1.292	0.2734	0.06915	0.1213
0.75	1.433	0.2082	0.03911	0.06314
0.80	1.596	0.1521	0.02061	0.03091
0.85	1.793	0.1040	0.009629	0.01353
0.90	2.052	0.06294	0.003578	0.004742
0.95	2.461	0.02836	0.0007505	0.0009439
1	∞	0	0	0

5. RESULTS AND DISCUSSION

Table 3 gives the force of repulsion by method III, which yields the most accurate results, for the sixty potential distributions available (see part I). The corresponding values for the force, as determined by method V, are shown for comparison. It should be observed that according to method V, the ratio f^*/τ depends on Φ and R^* but is independent of τ ; this is an approximation. The agreement between methods III and V is surprisingly good over a wide range of Φ , τ and R^* , although the error in method V clearly increases with decrease in τ and increases to a less degree when Φ or R^* become large.

TABLE 3. FORCE OF REPULSION BETWEEN TWO SPHERICAL PARTICLES

Evaluation by methods III and V of the quantity $f^*/2\pi\tau\Phi^2$ for various τ , Φ and $R^* = R - 2\tau$.

τ	R^*	Φ				
		0.50	1.00	1.50	2.00	3.00
		III				
1	2	0.8551	0.5004	0.2765	0.1486	0.0453
	4	0.8049	0.4144	0.2214	0.1208	0.0368
	6	0.6694	0.3090	0.1616	0.0883	0.0275
	8	0.5070	0.2209	0.1147	0.0630	0.0200
5	2	0.7802	0.5025	0.3173	0.1941	0.0708
	4	0.7404	0.3977	0.2337	0.1390	0.0508
	6	0.6098	0.2825	0.1583	0.0931	0.0343
	8	0.4568	0.1995	0.1080	0.0633	0.0235
15	2	0.7528	0.4943	0.3211	0.2057	0.0775
	4	0.7211	0.3941	0.2321	0.1418	0.0535
	6	0.5939	0.2794	0.1557	0.0933	0.0353
	8	0.4444	0.1939	0.1055	0.0628	0.0239
		V				
τ large	2	0.760	0.497	0.319	0.203	0.0794
	4	0.71	0.38 ₈	0.226	0.137	0.0522
	6	0.577	0.268	0.147	0.0863	0.0323
	8	0.422	0.179	0.0952	0.0553	0.0205

When integrating the expression for the force with respect to the separation R in method III an unknown additive constant was brought in, since the smallest value of the force was determined at a finite value of R . To overcome this difficulty we proceeded in the following way in the case of small τ . When R is sufficiently large the potential will be so small at any point in the median plane that the approximate linear Debye–Hückel equation may replace the Poisson–Boltzmann equation. Provided τ is not too large (less than 10, say) we may then assume linear superposition of the potentials due to the separate particles and so write the potential distribution on the median plane as

$$\phi = g(\tau, \Phi) \left[\frac{e^{-r'_1}}{r'_1} + \frac{e^{-r'_2}}{r'_2} \right], \quad (5.1)$$

where $g(\tau, \Phi)$ is some function of τ and Φ and r'_1 and r'_2 ($r'_1 = r'_2$) are the distances (in units of $1/\kappa$) of any point of the median plane from centres O and O' respectively. We may write (3.4) as

$$\begin{aligned} f^* &= \int_{S'_m} [|\nabla'\phi|^2 + 2(\cosh\phi - 1)] dS' \\ &\approx \int_{S'_m} [|\nabla'\phi|^2 + \phi^2] dS' = 2\pi \int_0^\infty \left[\left(\frac{d\phi}{d\rho'} \right)^2 + \phi^2 \right] \rho' d\rho'. \end{aligned} \quad (5.2)$$

Noting that (5.1) becomes

$$\phi = \frac{2g(\tau, \Phi)}{\sqrt{\{\rho'^2 + (\frac{1}{2}R')^2\}}} \exp \left[-\sqrt{\{\rho'^2 + (\frac{1}{2}R')^2\}} \right], \quad (5.3)$$

where $R' = \tau R$ is the separation, (4.2) is readily integrated and yields

$$f^* = 8\pi g^2(\tau, \Phi) \frac{e^{-R'}}{R'} \left(1 + \frac{1}{2R'} \right). \quad (5.4)$$

Integration of (5.4) yields $\Delta F^* = 8\pi g^2(\tau, \Phi) e^{-R'}/R'$. (5.5)

The function $g(\tau, \Phi)$ is then computed by substituting the numerical value of the force for the given Φ and τ at the largest value of R' . This method is applicable at $\tau = 1$ and $\tau = 5$, but not at $\tau = 15$, since the higher terms in the expansion for Φ of which (5.1) is the first term become important (cf. Verwey & Overbeek (1948)). For small Φ the results of Levine (1939) indicate that $g(\tau, \Phi) = \Phi\tau e^\tau$ very nearly and then (5.5) reduces to the expression derived by Verwey & Overbeek (1948, p. 149) for large R' and small Φ . At large τ , when (5.1) is no longer applicable, use is made of one of the three series expansions developed in the preceding section of the Derjaguin formula (4.1) (method V).

In table 4, the free energy is computed by method III for the sixty cases referred to above. The free energy at the largest separation is determined from (5.5) for $\tau = 1$ and 5 and by method V (i.e. from one of (4.3), (4.5) and (4.12)) at $\tau = 15$. Now according to the latter method, the ratio $\Delta F^*/\tau$ depends on Φ and R^* but is otherwise independent of τ ; in particular, it should take the same value at $\tau = 5$ and 15 for given Φ and R^* . But we see that the values given by (5.5) and method V for $\Delta F^*/\tau$ at $R^* = 3$ and $\tau = 5$ differ slightly. This indicates that at $\tau = 5$ the additive constant, which is required when integrating the force expression, may be somewhat in error in the last figure in table 4. This uncertainty could

be removed by extending the computations to larger values of the separation. In table 4 the results obtained by method III are also compared with the following:

(i) The series of Verwey & Overbeek (1948) which is the solution of the linear Debye-Hückel equation and is based on the expansion for the potential developed by Levine (1939) (to be referred to as method VI). This is applicable at small values of Φ , and it is seen that the agreement is fairly good for $\Phi = 2$, $\tau = 1$ but becomes worse as Φ or τ increases. This comparison is also illustrated in figure 1 for $\tau = 1$ and various Φ .

TABLE 4. FREE ENERGY OF INTERACTION

Evaluation by various methods of the quantity $\Delta F^*/4\pi\tau\Phi^2$.

Φ	$\tau(s-2)$	$\tau=1$		$\tau=5$		$\tau=15$	τ large	
		VI	I	VI	I	—	V	V
Φ small	0.00	0.658	—	0.768	—	—	—	0.693
	0.50	0.395	—	0.490	—	—	—	0.474
	1.00	0.222	—	0.304	—	—	—	0.313
	1.50	0.120	—	0.184	—	—	—	0.201
	2.00	0.066	—	0.110	—	—	—	0.127
	3.00	0.020	—	0.026	—	—	—	0.049
2	0.50	III 0.375	I 0.375†	III 0.416	I 0.416†	III 0.428	V _a 0.430	V 0.427
	1.00	0.211	0.221	0.260	0.230	0.271	0.276	0.272
	1.50	0.146	0.127	0.159	0.204	0.172	0.173	0.172
	2.00	0.065	0.081	0.097	0.181	0.107	0.107	0.107
	3.00	0.021	0.047	0.034	0.172	0.041	0.0408	0.0415
4	0.50	0.317	0.317†	0.325	—	0.329	0.288	0.319
	1.00	0.171	0.183	0.191	—	0.194	0.186	0.190
	1.50	0.094	0.111	0.113	—	0.118	0.116	0.115
	2.00	0.053	0.075	0.068	—	0.073	0.0717	0.0709
	3.00	0.017	0.057	0.024	—	0.027	0.0272	0.0271
6	0.50	0.240	0.334	0.232	—	0.232	—	0.223
	1.00	0.126	0.214	0.130	—	0.130	0.113	0.122
	1.50	0.069	0.136	0.076	—	0.077	0.0720	0.0725
	2.00	0.039	0.080	0.046	—	0.047	0.0447	0.0441
	3.00	0.013	0.000	0.016	—	0.017	0.0169	0.0168
8	0.50	0.173	—	0.164	—	0.161	—	0.148
	1.00	0.090	—	0.089	—	0.088	0.072	0.0792
	1.50	0.049	—	0.049	—	0.051	0.0456	0.0464
	2.00	0.028	—	0.031	—	0.031	0.0284	0.0281
	3.00	0.009	—	0.011	—	0.011	0.0107	0.0107

† Values adjusted by an additive constant to agree at $\tau(s-2) = 0.50$ with those obtained by method III.

(ii) The values of the free energy by the approximate method V of Derjaguin. When $\Phi = 2$, we used equation (4.5) (method V_b) and for larger values of Φ , equation (4.12) (method V_c). Just as in table 3, the agreement between methods III and V is in general good except at small τ . In figure 2 we illustrate the difference between these two methods.

(iii) The equation (4.3) for the free energy which should only hold for large R and τ (method V_a). It is observed that the agreement with method III is fairly good, even for values of R^* as low as 1.5.

(iv) The free energy determined directly by method I only in those cases where the results are not too grossly inaccurate. In table 5, the values of F^* obtained by methods I and II are compared with the (correct) values determined by method III. The values of $2F_0^*$, the corresponding quantity for two single particles, are also given to show the relative

magnitudes of F^* , $2F_0^*$ and the difference ΔF^* . The relative errors in F^* by methods I and II are not large for the values in table 3, but the error in ΔF^* becomes very large in general and the results are of little use, particularly by method II.

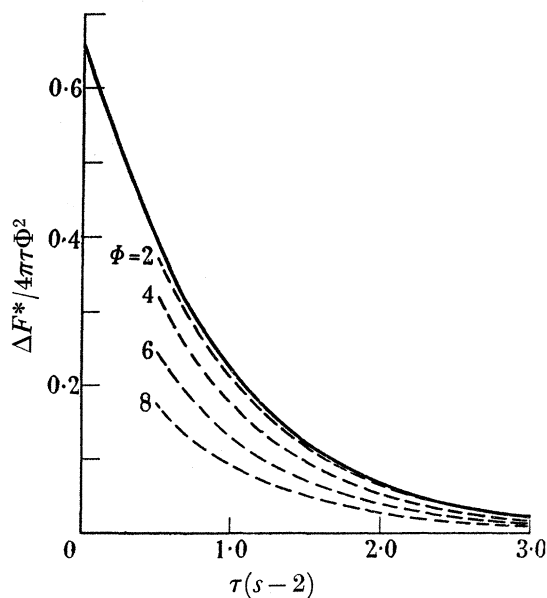


FIGURE 1. Comparison of methods III and VI for $\tau = 1$.
—, method VI (valid for $\Phi \ll 1$); ----, method III.

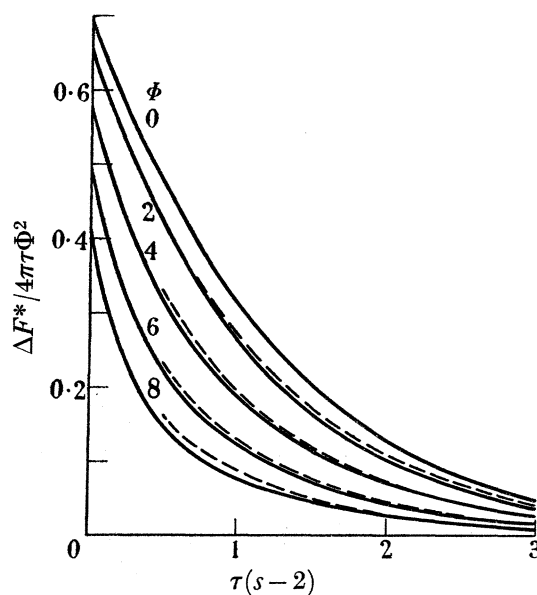


FIGURE 2. Comparison of methods III and V for $\tau = 15$.
—, method V; ----, method III.

In table 6 we compare methods III and IV for obtaining the force between the particles. Method IV is dependent on the values of the surface charge, and it has been explained in part I that the potential distribution is given on a mesh which is not suitable for accurate determination of the potential gradient at the particle surface. For $\Phi = 2$ the discrepancy is not great, but for $\Phi = 4$ the error in method IV increases, and it is of little use for the remainder of the cases presented in table 2.

The numerical results in part I can be utilized to investigate the nature of the approximations in method V in the following manner. According to (3.4), the force between the particles is determined solely by the potential distribution in the median plane. Now the model chosen in method V implies that the potential distribution is given approximately by the form (4.7), provided

$$\Theta = \frac{1}{2}[R' - 2\sqrt{(\tau^2 - \rho'^2)}] \quad (\rho' \leq \tau) \quad (5.6)$$

and $\psi_m = \psi_m(\rho')$ is the potential on the median plane at a distance ρ' from the line of centres. The formulae (4.7) and (5.6) define $\phi_m = \phi_m(\rho')$ as a function of ρ' in the range $0 \leq \rho' \leq \tau$.

TABLE 5. FREE ENERGY OF TWO SPHERES

τ	$\tau(s-2)$	Φ	$2F_0^*/4\pi$	$F^*/4\pi$		
				method I	method II	method III
1	0.5	2	16.49	14.8	14.8	15.1
		4	73.2	67.5	70.4	68.4
1	1.0	2	16.49	15.5	14.7	15.7
		4	73.2	69.6	69.3	70.5
5	0.5	2	255.8	239	245	247
		4	1245	1303	1280	1219
5	1.0	2	255.8	243	254	251
		4	1245	1338	1247	1230
15	0.5	2	2070	1758	2870	2045
		4	10370	12036	15100	10291

TABLE 6. FORCE OF REPULSION BETWEEN TWO SPHERES

Comparison of methods III and IV.

Φ	method	$\tau(s-2)$	$f^*/2\pi$				
			0.50	1.00	1.50	2.00	3.00
2	III		3.42	2.00	1.11	0.594	0.181
	IV		3.83	2.08	1.15	0.586	0.208
4	III		12.8	6.63	3.54	1.93	0.589
	IV		15.2	7.97	5.10	3.83	1.542

In figures 3 and 4 we have compared the function $\phi_m(\rho')/\Phi$ as calculated in part I, with that defined by (4.7) and (5.6), for $\tau = 5$ and 15 , $\Phi = 2$ and 8 and the smallest and largest separations considered. Since the formula (4.1) can be approximately expressed as

$$\Delta F^* = 2\pi \int_0^\tau \frac{\kappa}{nkT} \Delta F_p \{R' - 2\sqrt{(\tau^2 - \rho'^2)}\} \rho' d\rho' \quad (5.7)$$

(cf. Verwey & Overbeek 1948, p. 138), we have also plotted the integrand (a dimensionless quantity) as a function of ρ' . It is observed that for $\tau = 5$ and 15 the approximate value of $\phi_m(\rho')$, as given by (4.7) and (5.6), cannot be very different from the correct value provided $(\rho'/\tau)^2 \ll 1$. Furthermore, the approximate and accurate curves for $\phi_m(\rho')$ cross one another, which implies a partial cancellation of the errors introduced in method V. It is true that at larger ρ' , the formulae (4.7) and (5.6) yield rather poor results, which is to be expected, but then the contribution to the integrand in (5.7) from this range is small. It seems, therefore, that the success of method V is partly due to the fortunate compensation of errors.

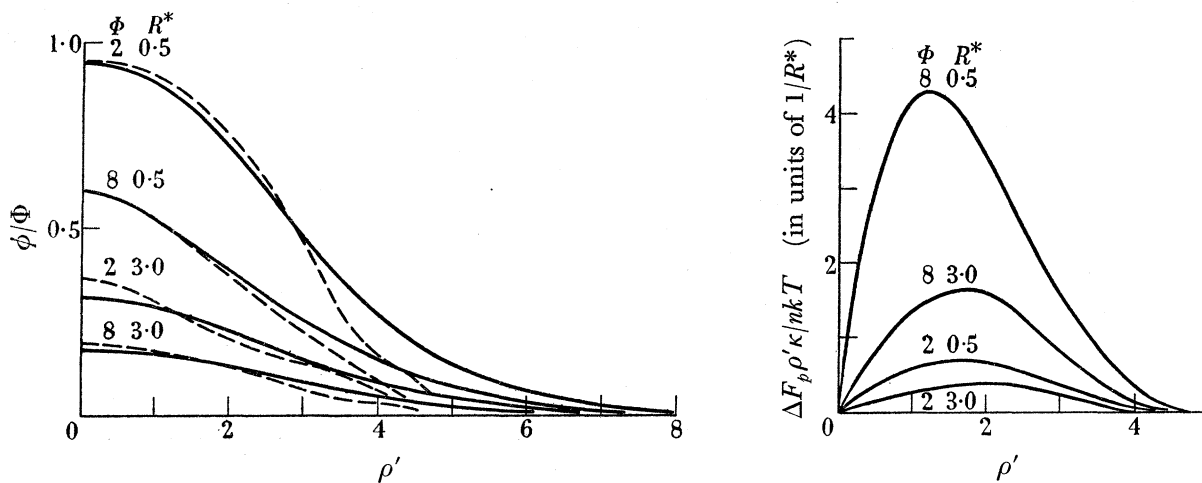


FIGURE 3. (Left) Comparison of potential distribution in the median plane for $\tau = 5$ and various Φ and R^* with the distribution defined by (4.11). —, actual distribution; ----, distribution defined by (4.11). (Right) Integrand in (4.12) for the same values of τ , Φ and R^* .

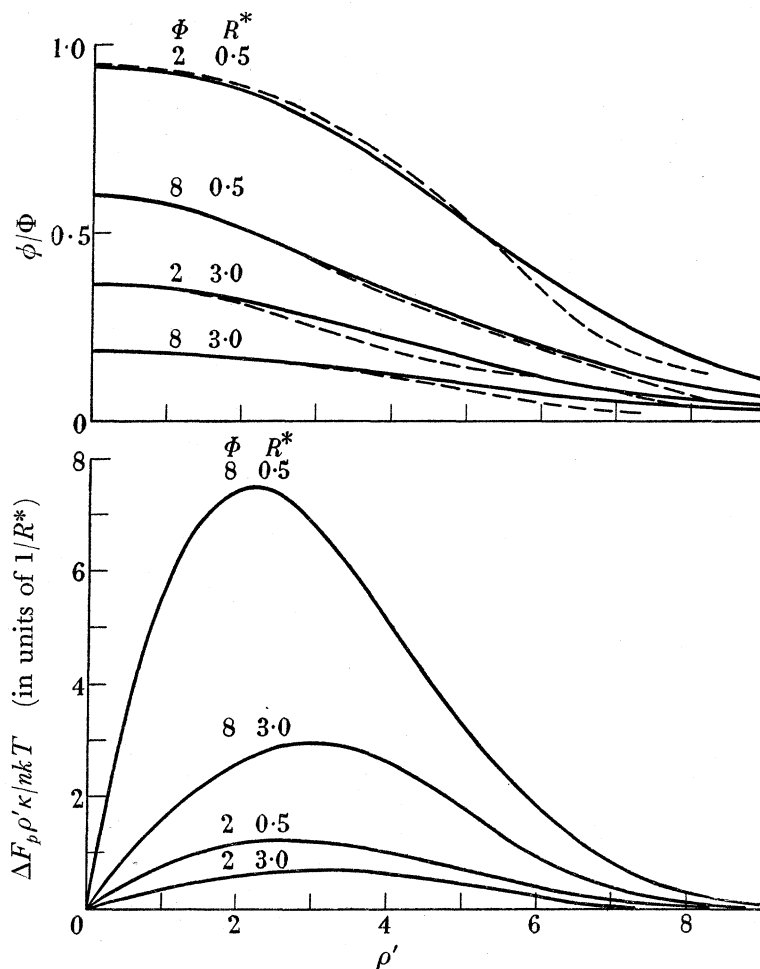


FIGURE 4. (Above) Comparison of potential distribution in the median plane for $\tau = 15$ and various Φ and R^* with the distribution defined by (4.11). —, actual distribution; ----, distribution defined by (4.11). (Below) Integrand in (4.12) for the same values of τ , Φ and R^* .

A summary of the description of the various methods is given below.

method	description	conditions for accuracy (with particular mesh employed in methods I to III)
I	free energy expressed as volume integral over diffuse ionic layers (equation (2.6))	small τ and R ($\tau < 3$, $\tau(s-2) < 1.5$ and $\Phi < 5$ say)
II	free energy expressed as integral over particle surface (equation (2.8))	same as I, but less accurate
III	force expressed as integral over the median plane (equation (3.5))	all values of parameters
IV	force expressed as integral over the particle surface (equation (3.6))	small Φ (≤ 2 , say)
V	method of Derjaguin—set of parallel rings which are sections of parallel plates (a) expansion at large distances (equation (4.3)) (b) expansion at small potentials (equation (4.5)) (c) expansion at large potentials (equation (4.12))	large τ (> 3 , say) large R ($\tau(s-2) \geq 1.5$) small Φ (≤ 2.5 , say) large Φ (> 2 , say)
VI	application of series solution of linear Debye-Hückel equation	small τ (< 3 , say) and small Φ (≤ 2)

We conclude with the following remarks. The free energy depends on four parameters, namely, the electrolyte concentration, the surface potential, the particle radius and the particle separation, and these parameters have a wide range of values. Furthermore, the surface potential need not be uniform or independent of the separation. This suggests that it would be more practical not to rely entirely on numerical computations, but, on the basis of the general theories already developed by various authors, to obtain approximate formulae valid for parts of the range of the above parameters. These methods could be used in conjunction with numerical methods which would no longer have to be applied over the whole range but only where the theoretical expressions are poor approximations. One such approach is method V, which has been examined in some detail in the present paper. Another possible method is based on the result that the Poisson-Boltzmann equation is the Euler differential equation which is obtained when the free-energy expression (2.1) is required to be an extremum, subject to the condition of uniform surface potential. This suggests that we choose a form for the potential distribution which depends on a number of suitably chosen parameters and then determine these parameters by some variant of the Rayleigh-Ritz method. Other approximate methods could doubtless be devised and it is hoped to consider such problems at a later date.

The authors wish to acknowledge their indebtedness to Mr D. F. Ferguson of the Department of Mathematics, University of Manchester, who carried out the greater part of the numerical computations in tables 1 and 2. They also wish to thank Mr D. C. Henry of the Department of Chemistry, University of Manchester, for his many valuable suggestions.

APPENDIX. GENERAL EXPRESSION FOR FORCE ON A PARTICLE

Let O and O' be convenient points fixed inside the particles P and P' respectively (which are of arbitrary shape and have a constant, uniform surface potential ψ_0), and let the vector \mathbf{s} denote the position of O relative to O' . Suppose now that the particle P is given a uniform infinitesimal translation $\delta\mathbf{s}$, but no rotation. We denote (i) the volume of the diffuse ionic atmosphere surrounding the two particles, which is not occupied by the particles in either

configuration, by V^* ; (ii) the volume which is vacated by P when O is displaced to $\mathbf{s} + \delta\mathbf{s}$ and which is occupied by the diffuse layer, by δV_1 ; and (iii) the corresponding volume vacated by the diffuse layer and occupied by the particle P , by δV_2 (see figure 5, where the particle P is a sphere and the displacement $\delta\mathbf{s}$ is along the line of centres so that $\delta s = \delta R$). Then in position \mathbf{s} of O , the volume V external to the two particles is $V^* + \delta V_2$, and in position $\mathbf{s} + \delta\mathbf{s}$ this volume is $V^* + \delta V_1$, where, of course, $\delta V_1 = \delta V_2$. The potential at any position \mathbf{r} in V relative to O' may be written as $\psi(\mathbf{r}, \mathbf{s})$; we are not concerned with the dependence of the potential on the mutual orientation of the two particles since this is kept fixed. When the position of O is changed to $\mathbf{s} + \delta\mathbf{s}$, the potential becomes $\psi(\mathbf{r}, \mathbf{s} + \delta\mathbf{s})$, which is expanded in the form

$$\psi(\mathbf{r}, \mathbf{s} + \delta\mathbf{s}) = \psi(\mathbf{r}, \mathbf{s}) + \psi_1(\mathbf{r}, \mathbf{s}) \delta s + O(\delta s)^2, \quad (\text{A } 1)$$

where δs is the magnitude of the vector $\delta\mathbf{s}$ and, of course, $\psi_1(\mathbf{r}, \mathbf{s})$ also depends on the direction of $\delta\mathbf{s}$. For brevity we shall write $\psi = \psi(\mathbf{r}, \mathbf{s})$ and $\psi_1 = \psi_1(\mathbf{r}, \mathbf{s})$. In the analysis that follows, it will be understood that we need only retain terms up to order δs .

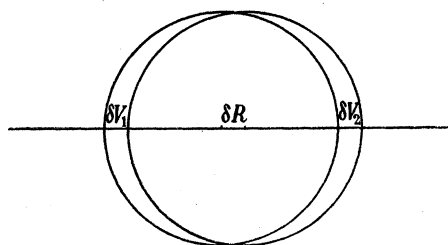


FIGURE 5

When O is displaced by $\delta\mathbf{s}$, the second term in the expression (2.2) for F changes by

$$\delta F_1 = -2nkT \left[\int_{V^* + \delta V_1} \left(\cosh \frac{ze}{kT} (\psi + \psi_1 \delta s) - 1 \right) dv - \int_{V^* + \delta V_2} \left(\cosh \frac{ze\psi}{kT} - 1 \right) dv \right]. \quad (\text{A } 2)$$

Now at any point in δV_1 or δV_2 the potential differs from ψ_0 by an amount of order δs . Hence the integral over δV_1 in (A 2) can be written as

$$-2nkT \delta V_1 \left(\cosh \frac{ze\psi_0}{kT} - 1 \right) (1 + O(\delta s)),$$

and the corresponding integral over δV_2 has the same form but with the opposite sign. Since $\delta V_1 = \delta V_2 = O(\delta s)$, the sum of the contributions from the volumes δV_1 and δV_2 on the right-hand side of (A 2) is of order $(\delta s)^2$. We are therefore left with the integrals over V^* and these yield

$$\delta F_1 = -2nkT \delta s \int_{V^*} \frac{ze\psi_1}{kT} \sinh \frac{ze\psi}{kT} dv = -\frac{\epsilon \delta s}{4\pi} \int_{V^*} \psi_1 \nabla^2 \psi dv, \quad (\text{A } 3)$$

since ψ satisfied the Poisson–Boltzmann equation.

Substituting (A 1) the first term on the right-hand side of (2.2) changes by

$$\delta F_2 = -\frac{\epsilon}{8\pi} \left[2\delta s \int_{V^*} (\nabla \psi \cdot \nabla \psi_1) dv - \int_{\delta V_1} |\nabla(\psi + \psi_1 \delta s)|^2 dv + \int_{\delta V_2} |\nabla \psi|^2 dv \right]. \quad (\text{A } 4)$$

The integrals over V^* in (A 3) and (A 4) may be combined to give

$$\frac{\epsilon \delta s}{4\pi} \int_{V^*} [\psi \nabla^2 \psi_1 - \psi_1 \nabla^2 \psi - \nabla \cdot (\psi \nabla \psi_1)] dv = \frac{\epsilon \delta s}{4\pi} \int_{S_p + S_p'} \psi_1 \frac{\partial \psi}{\partial n} dS, \quad (\text{A } 5)$$

transforming to a surface integral. Here S'_p is the surface of particle P' , S_p^* is the surface which bounds the volume swept out by particle P when it is displaced by $\delta\mathbf{s}$ and $\partial/\partial n$ denotes differentiation along the *outward* normal to these surfaces. On S'_p , $\psi_1 = 0$ and on S_p^* the form of ψ_1 may be obtained as follows. Consider a point N , say, which has a fixed position relative to O' and which is on the part of the surface S_p^* that forms a boundary of δV_1 . When O is in position \mathbf{s} , N is on the surface of P and therefore the potential at N is ψ_0 . When the particle P is given a uniform translation $\delta\mathbf{s}$, N becomes a point in the diffuse ionic layer and so the potential is less than ψ_0 , i.e. $\psi_1 < 0$. If \mathbf{n} denotes the unit outward normal vector to the surface S_p^* at N , then the normal distance of N from the surface of P when O has position $\mathbf{s} + \delta\mathbf{s}$ is given by $-\mathbf{n} \cdot \delta\mathbf{s}$. Hence noting that $\partial\psi/\partial n < 0$ at the particle surface, the change in the potential at N when O is displaced by $\delta\mathbf{s}$ is

$$\psi_1 \delta s = -(\partial\psi/\partial n) \mathbf{n} \cdot \delta\mathbf{s}. \quad (\text{A } 6)$$

A similar argument shows that (A 6) also represents the change with the displacement $\delta\mathbf{s}$ in the potential at a point on that part of S_p^* which is a boundary of δV_2 . It follows that the right-hand member of (A 5) may be written as $-2\mathbf{X} \cdot \delta\mathbf{s}$, where

$$\mathbf{X} = \frac{\epsilon}{8\pi} \int_{S_p} \left(\frac{\partial\psi}{\partial n}\right)^2 \mathbf{n} dS = \frac{\epsilon}{8\pi} \int_{S_p} E^2 \mathbf{n} dS. \quad (\text{A } 7)$$

We note that since terms of order $(\delta s)^2$ are neglected, the surface S_p^* may be replaced by S_p .

There remains to consider the integrals over δV_1 and δV_2 in (A 4). The integrands in both these integrals may be equated to E^2 . Since the particle P has been given a uniform translation $\delta\mathbf{s}$ without rotation, an element of volume in δV_1 may be written as $dv = -(\mathbf{n} \cdot \delta\mathbf{s}) dS$ and in δV_2 as $dv = (\mathbf{n} \cdot \delta\mathbf{s}) dS$, where dS is an element of surface on P . Thus, the sum of the two integrals over δV_1 and δV_2 in (A 4) is simply $\mathbf{X} \cdot \delta\mathbf{s}$ and so finally

$$\delta F = \delta F_1 + \delta F_2 = -\mathbf{X} \cdot \delta\mathbf{s}. \quad (\text{A } 8)$$

Since F is interpreted as the potential energy of interaction of the electric double layers of the two particles (ignoring the additive constant $2F_0$), it follows that \mathbf{X} is the (repulsive) force exerted on P by P_1 . We note that the surface integral on the right-hand side of (3.2) becomes identical with \mathbf{X} if S_p is chosen for S . Suppose now that (3.2) is applied to the case where S consists of S_p and S_c , where S_c is any closed surface surrounding P but excluding P' . We immediately derive the general expression for the force on the particle P , namely,

$$\mathbf{X} = \int_{S_c} \left[\frac{\epsilon}{4\pi} \{(\mathbf{E} \cdot \mathbf{n}) \mathbf{E} - \frac{1}{2} E^2 \mathbf{n}\} - (\Pi - \Pi_0) \mathbf{n} \right] dS, \quad (\text{A } 9)$$

where the unit vector \mathbf{n} is drawn outward to S_c . In the particular case of identical spherical particles we obtain the two equivalent expressions in (3.3), depending on whether S_c is chosen as the median plane S_m or as the particle surface S_p . Indeed, the formulae (3.3) apply to other particles of symmetrical shape (e.g. cylinder, cubes, spheroids), provided they are identical and are symmetrically orientated to one another. Also, it is readily shown that \mathbf{X} tends to zero as the separation of any two particles increases. For we need only apply (3.2) to the case of a single particle, where S consists of S_p and a large sphere, the radius of which becomes infinitely large; thus \mathbf{X} vanishes for a single particle.

Our discussion has been restricted to the case of a symmetrical binary electrolyte, but it is readily shown that the general expression derived for the force applies to a general electrolyte type. Furthermore, we may expect the general expression (A 9) for the force to be independent of the particular surface conditions, whereas the formula (2.1) for the free energy applies only when the surface potential is uniform and independent of separation. This property of the force has already been noted in special cases by Verwey & Overbeek (1948), Levine (1946) and Ikeda (1953), but we shall not attempt to prove it generally. Finally, one could extend the foregoing analysis to derive the torque acting on a particle, which is associated with its rotational motion.

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