

Double-layer Interaction between Spheres with Unequal Surface Potentials

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After a qualitative and quantitative comparison of various methods for calculating double-layer interaction the results of Hogg, Healy and Fuerstenau and those of Barouch, Matijević and coworkers on the energy of interaction between unequal spheres are dealt with. These results show unexpectedly large differences. The cause of these differences is found and after application of a necessary correction to the results of Barouch and Matijević the remaining differences are small, even for moderately large surface potentials.

In 1966 Hogg, Healy and Fuerstenau¹ (HHF) published a paper in which a theory for the double-layer interaction between spheres of unequal size and unequal surface potential is given, using the linear approximation of the Poisson–Boltzmann equation (PB equation), valid for small potentials, smaller than 25 mV. They derived a fairly simple equation for the free energy of interaction, which appeared to give quite reasonable results, even at potentials much higher than 25 mV. In 1978 Barouch, Matijević, Ring and Finlan² (BMRF) analysed the same problem, now using the full PB equation, and found results which differed rather markedly from those of HHF. This paper was challenged by Chan and White³ (CW), who suggested that the main cause of the difference between HHF and BMRF was due to an inappropriate truncation of a series expansion used by BMRF. Chan and Chan⁴ (CC) obtained a few exact numerical solutions of the full PB equation, compared these with the HHF and BMRF results and concluded ‘that any disagreement between ... HHF and BMRF must be due to errors in the BMRF result ...’.

Then in 1985 Barouch and Matijević published three papers, one with Wright as coauthor (BM, I,⁵ BMW, II,⁶ BM, III⁷) in which they gave a new analysis of the expression for the double-layer interaction energy already derived by BMRF² and found large deviations from the HHF results, in particular at separations between the spheres smaller than one Debye length ($1/\kappa$). They reject the criticism by CW³ and CC⁴ explicitly. Very recently Barouch, Matijević and Parsegian⁸ (BMP) described their earlier results as ‘an exact solution for the force between spheres ...’ and mention ‘at intermediate separations ... where force and energy go through extrema ... a qualitative difference’ is found with HHF.

This is a very unsatisfactory situation. On the one hand there is the critique by Chan and coauthors and the general feeling that HHF is correct at low potentials and still quite a good approximation at potentials of *ca.* 50 mV. On the other hand, the results of the elaborate and intricate calculations of Barouch, Matijević and coauthors show in quite a number of cases ‘a qualitative difference’ with HHF. I therefore decided to check the problem again and try to understand where the difference between BM and HHF came from. However, before considering the papers by BM and HHF in detail, a few general remarks are in order about some aspects of the problem, that evidently are not always fully recognized.

Fundamental Difficulty of the Problem

For two spheres in proximity no analytical solutions of the PB equation are known, not even for the linearized case, let alone for the full equation. Only approximate analytical or numerical solutions can be used. Moreover, for two particles with surface potentials of the same sign but different magnitude, the double-layer interaction changes from repulsive at large separations to attractive at short distances, owing to the fact that the proximity of the surface of high potential causes the charge of the low potential surface to change sign.

Remarkably enough the problem was already very fully treated by Derjaguin⁹ in 1954 but, unfortunately, this paper has not received as much attention as it deserved, possibly because in the words of HHF 'the solutions are extremely unwieldy'.

Methods for Calculating Interaction

The force on a particle can be seen as the sum of the Maxwell stress of the electric field and the hydrostatic pressure due to the increased concentration of ions (see Verwey and Overbeek, VO^{10a}). Derjaguin⁹ described the force for parallel flat surfaces and for convex surfaces with large radii of curvature, using the full PB equation, but also giving simplified equations valid for low surface potentials.

The free energy of interaction can be found by integrating the force from infinite separation to the actual distance between the particles (VO^{10b}), but also as the difference between the free energies of the double-layer system at the actual and at infinite distance. The force is completely determined by the electric potential field, independent of the boundary conditions (constant surface potential, constant surface charge or other), but the change of the force with distance does depend on these boundary conditions. The free energy depends on the choice of its zero and on the boundary conditions.

The free energy of the double layer contains four contributions. These are: the chemical free energy (due to adsorption or desorption) of the surface charge, the electrical energy of the surface charge, the electrical energy of the space charge in the solution and the entropy contribution due to the uneven distribution of ions in the solution. The free energy is most easily found by the use of an imaginary charging process, thus limiting the calculation to the surface charge or to the bulk charge, but including all the other contributions automatically.

If the particle charge, Q , is constant, the chemical term may be dropped and the free energy is simply $\int \psi_0(Q) dQ$, ψ_0 being the surface potential (see Overbeek, O^{11a}). For low surface potentials Q is proportional to ψ_0 and the free energy becomes $+\frac{1}{2}Q\psi_0$.

At constant surface potential, where the surface charge changes with the configuration, the chemical term has to be added, and the double-layer free energy, F , becomes

$$F = \int_0^{Q_{\text{final}}} \psi_0 dQ + \frac{Q}{e} \Delta\mu(\text{surface-bulk}) = \int \psi_0 dQ - \psi_0 Q = - \int_0^{\psi_0^{\text{final}}} Q d\psi_0 \quad (1)$$

where e is the elementary charge, $\Delta\mu$ is the difference in chemical potential of the ions responsible for the surface charge and, since equilibrium is supposed to occur at ψ_0 , $\Delta\mu = -e\psi_0$ (see O^{11b}). For low surface potentials F becomes $-\frac{1}{2}Q\psi_0$. The equality of the absolute values of the linearized double-layer free energies at constant charge and at constant potential has in some cases led to confusion.

For surface charge adjustment with a limited number of adsorption or desorption sites, equations become slightly more complicated because then $\Delta\mu$ is not constant. We shall not consider this case here.

HHF¹ used $F = -\frac{1}{2}Q\psi_0$, and since $Q = \text{capacity} \times \psi_0$, $F = -(\text{geometrical factor}) \times \epsilon_r \epsilon_0 \psi_0^2$, where ϵ_r is the relative dielectric constant of the solution and ϵ_0 is the permittivity of free space.

Table 1. Double-layer free energies per unit area divided by $\epsilon_r \epsilon_0 \kappa(kT/e)^2$ for a single flat double layer according to three different approaches.

$z \equiv e\psi_0/kT$	0.5	1.0	2.0	4.0
linear approximation, $-\frac{1}{2}z^2$ (used by HHF)	-0.125	-0.5	-2.0	-8.0
$-\int Q d\psi_0 \rightarrow -4(\cosh z/2 - 1)$ (exact equation)	-0.125 65	-0.510 50	-2.172 3	-11.048 8
$-\frac{1}{2}\int \psi_0 \sigma dA = -\frac{1}{2}Q\psi_0 \rightarrow -z \sinh z/2$ (equivalent to BMRF)	-0.126 31	-0.521 10	-2.350 4	-14.507 4

BMRF² state in their eqn (2.3) that the ‘electrostatic energy’, $E = +\frac{1}{2}\int \psi_0 \sigma dA$ (at constant ψ_0 equivalent to $\frac{1}{2}\psi_0 Q$), where σ is the surface charge density and A is the area of the surface. Then they replace σ by $-\epsilon_r \epsilon_0 \partial\psi/\partial n$, where $\partial\psi/\partial n$ is the normal derivative [their eqn (2.4)] and they set

$$\frac{\partial\psi}{\partial n} = \mathbf{n} \text{ grad } \psi; \quad \mathbf{n} = \frac{\text{grad } \psi}{|\text{grad } \psi|}$$

leading to their eqn (2.6):

$$\frac{\partial\psi}{\partial n} = |\text{grad } \psi|. \tag{2.6}$$

This equation should have contained a choice of sign, \pm , since the normal derivative in eqn (2.4) is the change of ψ when going from the surface to the solution (not to the interior of the particle), and obviously this change may be either positive or negative just as σ may be either negative or positive. The omission of the \pm sign in eqn (2.6) together with the later limitation to positive surface potentials then leads to the replacement of $E = +\frac{1}{2}\int \psi_0 \sigma dA$ by $E =$ the equivalent of $-\frac{1}{2}\int \psi_0 \sigma dA$ (see also CW³), which is then used in all further calculations (BMRF,² BM⁵⁻⁷). They calculate the potential gradient at the surface (proportional to σ) using the full PB equation. At low potentials their results should be nearly identical to those of HHF, whereas at high potentials a difference should show up, but then $-\frac{1}{2}\int \psi_0 \sigma dA (= -\frac{1}{2}Q\psi_0)$ is not necessarily closer to $-\int Q d\psi_0$ than the formula of HHF.

As a simple illustration we calculated the double-layer free energy for a single flat double layer, where exact equations are available, with the three different approaches (table 1). The correct values lie nearly halfway between the HHF and the BM approximations, but slightly closer to HHF.

Potential vs. Distance for Various Separations

In this section we shall mainly discuss the case of two parallel flat double layers.

When two double layers with equal surface potentials overlap, the potential has a minimum halfway between the plates. When the two surface potentials have the same sign, but a different magnitude, and the distance between the surfaces is not too small a similar minimum occurs, not half way, but closer to the surface with the smaller potential. This is illustrated in fig. 1(a). The figures have been drawn using eqn (2) of HHF, but the numbers would not be greatly different if the full PB equation had been used:

$$\psi = \frac{\psi_{01} \sinh \kappa(H-x) + \psi_{02} \sinh \kappa x}{\sinh \kappa H} \tag{2}$$

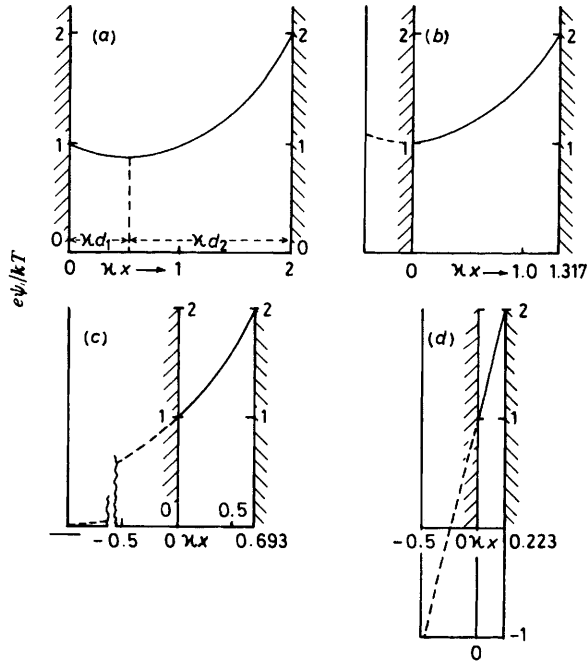


Fig. 1. Dimensionless potential, $e\psi/kT$, vs. dimensionless distance, κx , for two parallel flat surfaces at dimensionless surface potentials 1 and 2, respectively. Four typical cases are presented. (a) Fairly large separation; minimum in the potential between the surfaces; both surfaces carry positive charge; repulsion. (b) Shorter separation; minimum in the potential has just reached the low potential surface; no charge on surface 1; maximum repulsive force. (c) Separation so small that the extrapolated potential goes asymptotically to zero at $\kappa x \rightarrow \infty$; negative charge on surface 1; force between surfaces zero. (d) Separation still smaller; extrapolated potential goes to $-\infty$ at finite negative κx ; strong negative charge on surface 1; free energy of interaction goes through zero.

Table 2. Values of κH for which various quantities change sign (a) based on eqn (2), the linear approximation

ψ_{02}/ψ_{01}	$1 + \delta$	1.5	2.0	3.0	5.0	general
charge on surface 1 is zero	$(2\delta)^{1/2}$	0.962	1.317	1.763	2.292	$\text{arccosh}(\psi_{02}/\psi_{01})$
force is zero	δ	0.405	0.693	1.099	1.609	$\ln(\psi_{02}/\psi_{01})$
free energy of interaction is zero	$\delta^2/2$	0.080	0.223	0.511	0.955 ⁵	$\ln\left(\frac{\psi_{01}^2 + \psi_{02}^2}{2\psi_{01}\psi_{02}}\right)$

(b) comparison of results obtained with the linear approximation and with the full PB equation $e\psi_{0i}/kT \equiv z_i$

	$z_1 = 1; z_2 = 2$		$z_1 = 0.6; z_2 = 3$	
	linear approx.	full PB	linear approx.	full PB
charge on surface 1 is zero		1.317	1.179	2.086
force is zero		0.693	0.635	1.451

where ψ is the potential at a distance x from the surface with potential ψ_{01} and H is the distance between the two surfaces with potentials ψ_{01} and ψ_{02} , respectively. κ is the inverse Debye length

$$\kappa = \left(\frac{2F^2 c_0}{\epsilon_r \epsilon_0 RT} \right)^{\frac{1}{2}} \tag{3}$$

where F is the Faraday constant, R is the gas constant and c_0 is the molar concentration of the electrolyte, which is assumed to be symmetrical and monovalent.

When the distance between the surfaces is made smaller, a point is reached [see fig. 1(b)], where the minimum in the potential falls on the surface with potential ψ_{01} . Then its surface charge is zero, but the surfaces still repel one another. In this situation the repulsive force even reaches its maximum, since ψ_{01} is the maximum value that can be reached by the potential in the minimum and the repulsive force per unit area, p , is given by Langmuir,¹² VO^{10b} as

$$\begin{aligned} p &= 2c_0 RT [\cosh(e\psi_{\min}/kT) - 1] = \epsilon_r \epsilon_0 \kappa^2 \left(\frac{kT}{e} \right)^2 (\cosh u - 1) \\ &= [\text{for the case of fig. 1(b)}] \epsilon_r \epsilon_0 \kappa^2 \left(\frac{kT}{e} \right)^2 [\cosh(e\psi_{01}/kT) - 1] \end{aligned} \tag{4}$$

where ψ_{\min} is the potential in the minimum and $u = e\psi_{\min}/kT$. In Derjaguin's paper⁹ this maximum in the repulsive force is nicely shown in the figures, and also that its value depends only on the lower surface potential, since there $\psi_{\min} = \psi_{01}$.

At smaller distances than those in fig. 1(b), the surface charge on the first surface is reversed in sign, but the potential *vs.* distance curve can be extended to negative values of x , and as long as a minimum potential occurs in the prolonged curve, this ψ_{\min} may be used in eqn (4) to find the repulsive force between the surfaces.

At the separation shown in fig. 1(c), where the minimum has shifted to $x \rightarrow -\infty$ and $\psi_{\min} = 0$, the repulsive force is zero and a maximum occurs in the interaction free energy. At distances shorter than that in fig. 1(c) there is no minimum in the potential any more, the force becomes attractive and at the separation shown in fig. 1(d) the free energy of interaction goes through zero to end up at minus infinity at zero separation.

Table 2 illustrates how the separations at which the various sign reversals occur depend on the values of the two surface potentials.

The separations at which the reversals occur increase with the ratio ψ_{02}/ψ_{01} . At $e\psi_{02}/kT = 2$ or 3 the linear approximation gives reversal separations which are *ca.* 10% too high.

With two spherical particles, only the regions close to the axis of symmetry may show these reversals, whereas the parts of the surfaces farther away from the axis will be separated by larger distances and thus show no reversal. The net effect will be that the force and the free energy will change sign only at considerably smaller distances between the spherical surfaces than were found for parallel flat surfaces.

The Free Energy of Interaction

Parallel Flat Surfaces, High Surface Potentials, Large Distances

From the potential distribution given in eqn (2) HHF derive an expression for the free energy of interaction per unit area of two parallel flat double layers, exact in the linear approximation and given by

$$\begin{aligned} V_{\text{HHF}} &= 2\epsilon_r \epsilon_0 \kappa \psi_{01} \psi_{02} \exp(-\kappa H) \left(\frac{1 - \frac{\psi_{01}^2 + \psi_{02}^2}{2\psi_{01}\psi_{02}} \exp(-\kappa H)}{1 - \exp(-2\kappa H)} \right) \\ &\approx 2\epsilon_r \epsilon_0 \kappa \psi_{01} \psi_{02} \exp(-\kappa H) \text{ (for large } \kappa H \text{)}. \end{aligned} \tag{5}$$

For high potentials expressions for the free energy of interaction become cumbersome and contain elliptic integrals (VO^{10e}), but for high surface potentials and small interaction, interesting comparisons can be made. For large separations correct values for the potential around the minimum are obtained by superimposing the potential distributions of the two separate double layers, each stretching out to infinity, on one another. The following expressions are exact in the limit, $\kappa H \rightarrow \infty$. Henceforth we shall use $y_i = e\psi_i/kT$; $z_i = e\psi_{0i}/kT$; $\gamma_i = \tanh(z_i/4)$ and $i = 1$ or 2 :

$$\tanh(y_1/4) = \tanh(z_1/4) \exp(-\kappa x)$$

and
$$\tanh(y_2/4) = \tanh(z_2/4) \exp[-\kappa(H-x)]. \tag{6}$$

For small interactions we thus find

$$y = y_1 + y_2 = 4\gamma_1 \exp(-\kappa x) + 4\gamma_2 \exp[-\kappa(H-x)] \tag{7}$$

which has a minimum $y_{\min} \equiv u$ when $y_1 = y_2$ and consequently

$$\exp(-\kappa x_{\min}) = (\gamma_2/\gamma_1)^{1/2} \exp(-\kappa H/2) \tag{8}$$

and thus
$$u = 8(\gamma_1 \gamma_2)^{1/2} \exp(-\kappa H/2). \tag{9}$$

Combining this expression with eqn (4) for the repulsive force per unit area and integrating the force from $H = \infty$ to $H = H$, we find for the free energy of interaction per unit area

$$V_{ov} = 2\epsilon_r \epsilon_0 \kappa (kT/e)^2 (16\gamma_1 \gamma_2) \exp(-\kappa H). \tag{10}$$

This differs from V_{HHF} by the replacement of $\psi_{01} \psi_{02}$ by $16(kT/e)^2 \gamma_1 \gamma_2$.

An analogous equation for BM conditions is obtained as follows. They would have^{2,5} for the energy of interaction per unit area of two parallel surfaces

$$E_{BM} = -(\frac{1}{2}\sigma_1 \psi_{01} + \frac{1}{2}\sigma_2 \psi_{02}) + [\frac{1}{2}\sigma_1(H \rightarrow \infty) \psi_{01} + \frac{1}{2}\sigma_2(H \rightarrow \infty) \psi_{02}] \tag{11}$$

where σ_i is the charge per unit area of surface i . With

$$\sigma_1 = -\epsilon_r \epsilon_0 (d\psi_1/dx)_{x=0}, \quad \sigma_2 = +\epsilon_r \epsilon_0 (d\psi_2/dx)_{x=H}$$

and
$$(d\psi/dx)_{x=0, x=H} = \mp (kT/e) \kappa (2 \cosh z_i - 2 \cosh u)^{1/2} \tag{12}$$

where the minus sign is good for $x = 0$ and the plus sign for $x = H$, we find easily

$$\begin{aligned} E_{BM} &= \frac{1}{2}\epsilon_r \epsilon_0 \kappa (kT/e) (\psi_{01} \{2 \sinh(z_1/2) - 2 \sinh(z_1/2) [1 - \sinh^2(u/2)/\sinh^2(z_1/2)]^{1/2}\} \\ &\quad + \psi_{02} \{2 \sinh(z_2/2) - 2 \sinh(z_2/2) [1 - \sinh^2(u/2)/\sinh^2(z_2/2)]^{1/2}\}) \\ &\approx \frac{1}{2}\epsilon_r \epsilon_0 \kappa (kT/e)^2 \left(\frac{z_1}{\sinh(z_1/2)} + \frac{z_2}{\sinh(z_2/2)} \right) \frac{u^2}{4} \text{ (for small } u, \text{ large } \kappa H). \end{aligned} \tag{13}$$

With u as found in eqn (9) we have

$$E_{BM} = 2\epsilon_r \epsilon_0 \kappa (kT/e)^2 \left(\frac{z_1/4}{\sinh(z_1/2)} + \frac{z_2/4}{\sinh(z_2/2)} \right) [16\gamma_1 \gamma_2 \exp(-\kappa H)] \tag{14}$$

differs from V_{ov} by the factor with $[z_i/4 \sinh(z_i/2)]$.

In table 3 results are given for a few typical cases and we also give general expressions for the ratio of the various free energies of interaction. Again the correct expression based on $-\int Q d\psi_0$ is *ca.* half way between the linear approximation (HHF) and the BM results, but now HHF leads to the largest repulsion and BM to the smallest.

Table 3. Free energy of interaction per unit area of two parallel flat double layers divided by $2\epsilon_r \epsilon_0 \kappa(kT/e)^2 \exp(-\kappa H)$ for large separation

approximate ratio to $16\gamma_1 \gamma_2$	$z_1 z_2^a$	$\frac{z_1}{4 \sinh z_1/2} + \frac{z_2}{4 \sinh z_2/2}$	$\frac{16\gamma_1 \gamma_2^b}{1}$	$\frac{16\gamma_1 \gamma_2^c}{1 - \frac{z_1^2 + z_2^2}{48} \left(1 - \frac{7(z_1^2 + z_2^2)}{240} + \frac{7z_1^2 z_2^2}{120(z_1^2 + z_2^2)} \right)}$
$z_1 = 1; z_2 = 2$	2		1.811	1.639
$z_1 = 0.6; z_2 = 3$	1.8		1.513	1.278
$z_1 = 5; z_2 = 5$	25		11.513	4.757
$z_1 = 8; z_2 = 8$	64		14.870	2.179

^a HHF. ^b This paper. ^c BM.

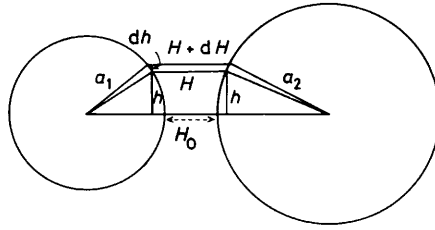


Fig. 2. The Derjaguin method for finding the interaction between spheres; see text, especially eqn (15).

Parallel Flat Surfaces, Small Distances

The HHF solution for the free energy of interaction, eqn (5), remains valid and is exact within the limitations of the linear approximation.

In the BM approach based on $-\frac{1}{2}\sigma\psi_0$ the interaction of flat surfaces is implicit in their treatment of the interaction of spheres.^{2,5,6} Unfortunately, a solution, other than numerical, based on $-\int\sigma d\psi_0$ is not available, since it requires the integration of eqn (12) for σ with respect to z_i , and u is a complicated function of z_1 and z_2 . The best way to solve the problem appears to be the use of the charging process of the ions in the solution, rather than on the surface, as was used by VO^{10d} for the symmetric case; however, since this involves a great deal of calculation we will not do this now, but switch to spherical particles.

Interaction between Spherical Particles

In the absence of a closed solution of the PB equation for spheres, HHF used the method proposed by Derjaguin¹³ in 1934 for deriving the interaction between spheres from that between flat surfaces. In this method the interaction (force or energy) of spheres is supposed to be built up from the interaction of pairs of rings with radius h , thickness dh , at a distance H , the rings interacting as if they were parallel flat surfaces with the same area and distance as illustrated in fig. 2 and in the equation

$$V_R = \int_{h=0}^{h=\text{large}} 2\pi h V(\text{flat}) dh \tag{15}$$

where V_R is the interaction between two spheres, $V(\text{flat})$ is the interaction per unit area of parallel surfaces and the upper limit of integration is so large that at the corresponding distance H interaction is negligible. The two conditions, viz. the field lines are virtually parallel and the maximum H is much smaller than the radius, limit the applicability of the Derjaguin method to large values of κa (say κa is 10 or more) and to $H_0 \ll a_1, a_2$. To a reasonable approximation

$$\left(\frac{1}{a_1} + \frac{1}{a_2}\right) h dh = dH \tag{16}$$

and thus eqn (15) can be transformed into

$$V_R = 2\pi \frac{a_1 a_2}{a_1 + a_2} \int_{H_0}^{\infty} V(h) dH. \tag{17}$$

With this equation and $V_{\text{HHF}}(H)$ from eqn (5) the free energy of interaction of two spheres becomes

$$V_{R, \text{HHF}} = \pi \frac{a_1 a_2}{a_1 + a_2} \epsilon_r \epsilon_0 \{ (\psi_{01} + \psi_{02})^2 \ln [1 + \exp(-\kappa H_0)] + (\psi_{02} - \psi_{01})^2 \ln [1 - \exp(-\kappa H_0)] \}. \quad (18)$$

This equation contains all the essentials of interaction and is exact for sufficiently large κa_1 and κa_2 . The free energy goes through zero at much lower distances H_0 than for flat surfaces. For $\psi_{02} = 2\psi_{01}$ the reversal distance is $0.001973/\kappa$ as compared to $0.223/\kappa$ for flat surfaces.

If κa_1 and/or κa_2 are not very large, eqn (16) can be slightly improved to

$$h \, dh [(a_1^2 - h^2)^{-\frac{1}{2}} + (a_2^2 - h^2)^{-\frac{1}{2}}] = dH$$

or approximately to

$$h \, dh = \frac{a_1 a_2}{a_1 + a_2} dH \left(1 - \frac{h^2}{2} \left(\frac{1}{a_1^2} - \frac{1}{a_1 a_2} + \frac{1}{a_2^2} \right) \right) \approx \frac{a_1 a_2}{a_1 + a_2} dH \left(1 - \frac{1}{\kappa a_1} \right) \quad (19)$$

where a_1 is the radius of the smaller sphere, and it is taken into account that most of the interaction takes place at $\kappa^2 h^2 < 2\kappa a_1$. Thus, apart from the influence of the actual curvature of the field lines, the classical Derjaguin result, eqn (17), and thus $V_{R, \text{HHF}}$, eqn (18), are too large by a factor of the order of $(1 + 1/\kappa a_1)$.

Ohshima, Chan, Healy and White¹⁴ (OCHW) took the curvature of the field lines into account and calculated a correction on $V_{R, \text{HHF}}$ still smaller than, but of the same sign as that found above. Barouch, Matijević and coworkers^{2,5,6} tackled the interaction of spheres in a rather different way, but Chan and White³ showed that their method is in the first approximation, *i.e.* neglecting $1/\kappa a$ corrections, equivalent to the Derjaguin method. BMRF² neglect the curvature of the field lines, calculate the potential gradient at the surface (proportional to the surface charge densities σ_1 and σ_2) for each h (see fig. 2, and note that BM and coworkers call r what we call h here) and then find the interaction $E_{R, \text{BM}}$ as

$$E_{R, \text{BM}} = \int_0^{a_1, a_2} \left(-\frac{1}{2} \psi_{01} \frac{[\sigma_1 - \sigma_1(H \rightarrow \infty)]}{(1 - h^2/a_1^2)^{\frac{1}{2}}} - \frac{1}{2} \psi_{02} \frac{[\sigma_2 - \sigma_2(H \rightarrow \infty)]}{(1 - h^2/a_2^2)^{\frac{1}{2}}} \right) 2\pi h \, dh \quad (20)$$

where the factors $(1 - h^2/a_i^2)^{-\frac{1}{2}}$ take into account that the surfaces of the spheres are not exactly perpendicular to the axis of symmetry. I have written

$$\sigma_{1,2} = -\epsilon_r \epsilon_0 (\partial\psi/\partial n)_{1,2} = \pm \epsilon_r \epsilon_0 \kappa \frac{kT}{e} [2 \cosh z_{1,2} - 2\phi(H)]^{\frac{1}{2}} \quad (21)$$

to bring out the parallel with the treatment for flat surfaces in eqn (11) and (12). The integration constant $\phi(H)$ is equal to $\cosh u$ when the potential has a minimum between or at the low potential side of the surfaces, but $\phi(H) < 1$ and may even be negative when the ϕ vs. x curve [see fig. 1(d)] drops to $-\infty$. The use of the sign for σ is tricky. If both surface potentials are positive, σ_2 is always positive ($|\psi_{02}| > |\psi_{01}|$), but σ_1 is positive when a minimum potential exists between the surfaces, otherwise σ_1 is negative, as should be clear from fig. 1. For negative surface potentials the signs of σ are just reversed.

The relation between H and ϕ is found from

$$H = \int_0^H dx = \int_{z_1}^{z_2} \frac{dy}{dy/dx} = \int_{z_1}^{z_2} \frac{dy}{\kappa [2 \cosh y - 2\phi(H)]^{\frac{1}{2}}} \quad (22)$$

in cases in which the potential increases monotonically with x [fig. 1(b)–(d)], but when

there is a potential minimum between the surfaces [fig. 1(a)] eqn (22) has to be modified to

$$H = \int_0^{x_{\min}} dx + \int_{x_{\min}}^H dx = - \int_{z_1}^u \frac{dy}{\kappa[2 \cosh y - 2 \cosh u(H)]^{\frac{1}{2}}} + \int_u^{z_2} \frac{dy}{\kappa[2 \cosh y - 2 \cosh u(H)]^{\frac{1}{2}}} \quad (23)$$

where ϕ has been interpreted as $\cosh u$.

For the integration of eqn (20) and (21) a relation between H and h is required, for which Barouch, Matijević and coworkers use the integrated form of eqn (16):

$$\frac{h^2}{2} \left(\frac{1}{a_1} + \frac{1}{a_2} \right) = H - H_0. \quad (24)$$

In eqn (20) it has been taken into account that the surfaces of the sphere rings are slightly larger than $2\pi h dh$. Similarly in eqn (21) it should have been taken into account that σ is proportional to the potential gradient normal to the equipotential surface and therefore larger by a factor $(1 - h^2/a_i^2)^{-\frac{1}{2}}$ than the value given in eqn (21). The omission of this factor makes $E_{R, BM}$ slightly lower than it should have been.

In BM^5 and BMW^6 the integrations of eqn (20)–(23) are carried out in detail, transforming the integrals in eqn (22) and (23) to standard elliptic integrals and switching from h to ϕ as the independent variable in eqn (20) and (21). Two sets of final equations are generated, one for the case with a minimum potential between the surfaces for all values of h . This one is straightforward, and the results are correct, apart from the use of $-\frac{1}{2} \int \psi_0 \sigma dA$ instead of $-\int Q d\psi_0$, and for the distances involved and low potentials the results are not too far from those of HHF. The very large deviations found for high potentials (fig. 8 in BM^7) are in line with our discussion in the section Parallel Flat Surfaces, High Surface Potential, Large Distances and table 3.

The other group of cases (no potential minimum between the surfaces at least for small h) is complicated. The integral for the energy [eqn (20)] has to be split into two integrals from 0 to h_c and from h_c to higher h , where h_c is the radius of the ring where the surface charge on surface 1 changes sign [fig. 1(b)] and therefore $\phi_c = \cosh z_1$. The relation between ϕ and H is found from eqn (22), which can be converted into standard elliptic integrals, but the exact transformation is different for different ranges of ϕ (see BMW^6). Taking all this into account, the actual integration of eqn (20) and (21) after switching from h to ϕ as the integration variable is straightforward, but it has to be carried out numerically, as dealt with in detail in BMW^6 .

Unfortunately, BM^5 and BMW^6 did not change the sign of σ at $h < h_c$ in accordance with their omission of the \pm sign in eqn (2.6), thus making their interaction energy too low by twice the absolute value of the terms involved at all separations $H_0 < h_c$. It is just at these short distances that the striking differences with HHF were found. To make the point more explicit, we give the relevant equations from Barouch and Matijević⁵ and indicate the changes of sign that have to be made. The BM equations have been recast using the symbols used in this paper. Their eqn (5.3) reads

$$E_{R, BM} = \epsilon_r \epsilon_0 \left(\frac{kT}{e} \right)^2 \pi \sqrt{2} \left[-a_1 z_1 \int_0^{\alpha_1} \left(\frac{[\cosh z_1 - \phi(H)]^{\frac{1}{2}} - (\cosh z_1 - 1)^{\frac{1}{2}}}{[(\kappa a_1)^2 - (\kappa h)^2]^{\frac{1}{2}}} \right) \right. \\ \left. \times (\kappa h) d(\kappa h) - a_2 z_2 \int_0^{\alpha_2} \left(\frac{[\cosh z_2 - \phi(H)]^{\frac{1}{2}} - (\cosh z_2 - 1)^{\frac{1}{2}}}{[(\kappa a_2)^2 - (\kappa h)^2]^{\frac{1}{2}}} \right) (\kappa h) d(\kappa h) \right]. \quad (25)$$

They integrate eqn (5.3) by parts to obtain their eqn (5.7). However, before this is done

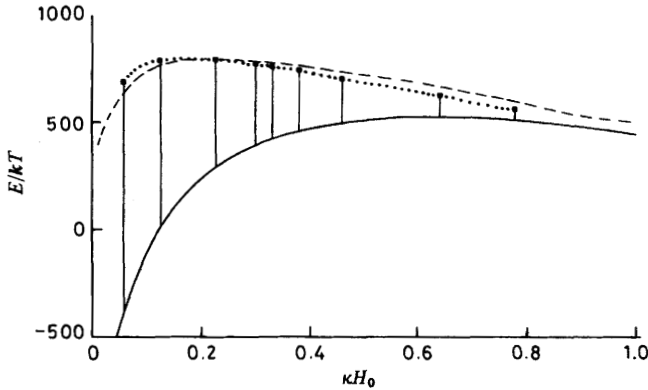


Fig. 3. Free energy of interaction of two spheres, $\psi_{01} = 25$ mV, $\psi_{02} = 50$ mV; $\kappa a_1 = 10, \kappa a_2 = 20$ vs. dimensionless shortest distance κH_0 ($\kappa = 10^7 \text{ m}^{-1}$). Figure redrawn from Barouch and Matijević.⁷ HHF according to eqn (18), PB equation linearized. BM as given in ref. (7) using the BM eqn (5.13). BM corrected according to eqn (27) and (28). See text. (---), HHF, (—) BM, (···) BM corrected.

the first integral should have been split at $h = h_c$ and the sign of $[\cosh z_1 - \phi(H)]^{\frac{1}{2}}$ should have been changed to $-[\cosh z_1 - \phi(H)]^{\frac{1}{2}}$, leading to

$$\begin{aligned}
 E_{R, \text{BM}}(\text{corrected}) = \epsilon_r \epsilon_0 \left(\frac{kT}{e}\right)^2 \pi \sqrt{2} & \left[a_1 z_1 \int_0^{\kappa h_c} \left(\frac{(\cosh z_1 - 1)^{\frac{1}{2}} + [\cosh z_1 - \phi(H)]^{\frac{1}{2}}}{[(\kappa a_1)^2 - (\kappa h)^2]^{\frac{1}{2}}} \right) \right. \\
 & \times (\kappa h) d(\kappa h) \\
 & + a_1 z_1 \int_{\kappa h_c}^{\kappa a_1} \left(\frac{(\cosh z_1 - 1)^{\frac{1}{2}} - [\cosh z_1 - \phi(H)]^{\frac{1}{2}}}{[(\kappa a_1)^2 - (\kappa h)^2]^{\frac{1}{2}}} \right) (\kappa h) d(\kappa h) \\
 & \left. + a_2 z_2 \int_0^{\kappa a_2} \left(\frac{(\cosh z_2 - 1)^{\frac{1}{2}} - [\cosh z_2 - \phi(H)]^{\frac{1}{2}}}{[(\kappa a_2)^2 - (\kappa h)^2]^{\frac{1}{2}}} \right) (\kappa h) d(\kappa h) \right] \quad (26)
 \end{aligned}$$

Integration by parts then gives eqn (27), which should replace BM eqn (5.13) and BMW eqn (2).

$$\begin{aligned}
 E_{R, \text{BM}}(\text{corrected}) = \epsilon_r \epsilon_0 \left(\frac{kT}{e}\right)^2 \pi \sqrt{2} & \left(a_1 z_1 \frac{\kappa a_1 [\phi(H_0) - 1]}{(\cosh z_1 - 1)^{\frac{1}{2}} \overrightarrow{[\cosh z_1 - \phi(H_0)]^{\frac{1}{2}}}} \right. \\
 & + a_2 z_2 \frac{\kappa a_2 [\phi(H_0) - 1]}{(\cosh z_2 - 1)^{\frac{1}{2}} + [\cosh z_2 - \phi(H_0)]^{\frac{1}{2}}} \\
 & - \frac{a_1 z_1}{2} \int_{\phi(H_0)}^{\cosh z_1} \frac{[(\kappa a_1)^2 - (\kappa h)^2]^{\frac{1}{2}}}{(\cosh z_1 - \phi)^{\frac{1}{2}}} d\phi \\
 & + \frac{a_1 z_1}{2} \int_{\cosh z_1}^{\phi \left[H - H_0 + \frac{a_1}{2} \left(1 + \frac{a_1}{a_2} \right) \right]} \frac{[(\kappa a_1)^2 - (\kappa h)^2]^{\frac{1}{2}}}{(\cosh z_1 - \phi)^{\frac{1}{2}}} d\phi \\
 & \left. + \frac{a_2 z_2}{2} \int_{\phi(H - H_0)}^{\phi \left[H - H_0 + \frac{a_2}{2} \left(1 + \frac{a_2}{a_1} \right) \right]} \frac{[(\kappa a_2)^2 - (\kappa h)^2]^{\frac{1}{2}}}{(\cosh z_2 - \phi)^{\frac{1}{2}}} d\phi \right) \quad (27)
 \end{aligned}$$

Ultimately this error in sign causes $E_{R, BM}$ as used in the BM papers to be too low by an amount [cf. eqn (25) and (26)] $\Delta E_{R, BM}$

$$\Delta E_{R, BM} = \varepsilon_r \varepsilon_0 \left(\frac{kT}{e} \right)^2 \pi \sqrt{2} \times 2a_1 z_1 \int_{h=0}^{h=h_c} \frac{(\cosh z_1 - \phi)^{\frac{1}{2}}}{[(\kappa a_1)^2 - (\kappa h)^2]^{\frac{1}{2}}} (\kappa h) d(\kappa h). \quad (28)$$

In order to give at least an impression of the quantitative effect of this correction, I roughly calculated it for the case $\psi_{01} = 25$ mV, $\psi_{02} = 50$ mV, $\kappa a_1 = 10$ and $\kappa a_2 = 20$, as drawn in the BM III fig. 1, in the following way. Using tables of elliptic integrals I calculated the relation between ϕ , varying from -135 to $+1.5116$ and κH , varying from 0.0587 to 1.185 at *ca.* 15 points, using eqn (22). Using *ca.* 10 of these values of κH for κH_0 I calculated h^2 corresponding to $H - H_0$ using eqn (24). Then I plotted the integrand of eqn (28) against $(\kappa h)^2$ and carried out the integration graphically. The final results expressed as $\Delta E_{R, BM}/kT$ are plotted in fig. 3 as additions to the line copied from the BM paper,⁷ and the corrected $E_{R, BM}$ values come quite close to the V_{HHF} values plotted in the same figure.

Conclusions

It is stressed that the free energy of a double-layer system under conditions of constant surface potential (*i.e.* the ions carrying the surface charge are in equilibrium with an excess of similar ions in the solution) is given by $-\int Q d\psi_0$ [eqn (1)].

The remarkable success of the linearized Poisson-Boltzmann equation in the treatment of the free energy of the double layer and of double-layer interaction even at dimensionless surface potentials of 2 (*ca.* 50 mV) is due to the fact that the first correction factor is $(1 \pm z^2/48)$.

The expressions, derived from the equivalent of $-\frac{1}{2} \int \sigma \psi_0 dA$ ($= -\frac{1}{2} Q \psi_0$ if ψ_0 is constant) as proposed by Barouch, Matijević and coworkers deviate in the first approximation from the correct expressions derived from $-\int Q d\psi_0$ by a factor $(1 \mp z^2/48)$, and are thus in this respect neither better nor worse than the linear approximation, but the deviations have the opposite sign.

The BM results published in ref. (5)–(8) are marred by an error of calculation which invalidates their results at separations below critical separation [see fig. 1(b) and eqn (26)], and in particular invalidates their suggestion that the true interaction shows a qualitative difference with the results of Hogg *et al.*,¹ who applied the linearized PB equation.

There is no profit in continuing calculations on double-layer interaction based on $-\frac{1}{2} Q \psi_0$ at high surface potentials. The method is much more complicated than that based on the linearized PB equation, and the results are not essentially closer to the true value.

Further progress in this field for moderate and high potentials will require solution of the integral $-\int Q d\psi_0$ or, equivalently, application of an imaginary charging process for the ions in solution, or integrating the force from infinity to the distance under consideration.

As long as κa is large enough ($\kappa a \gg 10$) the Derjaguin method is excellent for transforming the interaction of flat surfaces to that between curved surfaces.

For small κa and high potentials no analytical solutions or suitable series expansions are available. The only known way out at this moment is a computer solution of the full PB equation for the relevant geometry, and after that carrying out $-\int Q d\psi_0$ or one of its equivalents or (this would be a new method) calculating the field energy, the entropy of the uneven distribution of the ions and of the adsorption or dissociation free energy.

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